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M.S. Chouhan
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for JEE
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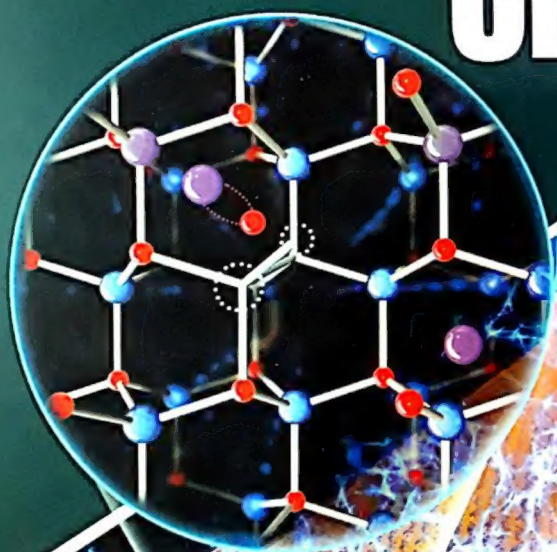

About the Author

Mahendra Singh Chouhan (MSC Sir) is a renowned name in the realm of Organic Chemistry. Through a Chemical Engineer from Mumbai University, his great passion for the subject led him to impart guidance to IIT-JEE aspirants on a regular basis. His in depth knowledge and vast experience has helped innumerable students to achieve their dream of excelling at IIT, JEE and other such tough challenges.

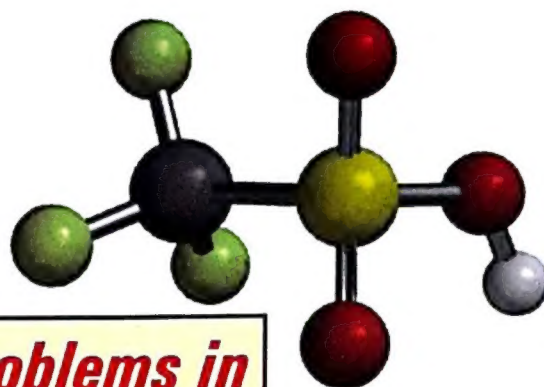
He has launched a website to extend the benefits of his expertise beyond the geographical barriers to all those who dare to dream and seek - **www.iitjeeorganic.com**.

The website provides expert guidance in all the areas of the subject in a most skillful manner. There are quizzes, challenging questions, notes, e-books and videos etc. This website is a complete guide in itself for organic chemistry and has been designed for IIT-JEE aspirants, keeping in mind the various syllabi and CBSE.

Highly recommended for the high flyers.

Advanced Problems in

ORGANIC CHEMISTRY

for

by:

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A few words to the JEE Aspirants

Dear JEE aspirants,

I hope that this collection of problems will surely help you during your preparation for JEE. In this book, each chapter consists of two levels :

Level 1 - includes the problems having only one option correct. These problems are based on different facts and their twists.

Level 2 - includes unique approach which may be used to solve the problems altogether different from the prevailing trend followed by JEE. These approaches will undoubtedly help you in the quick revision of the key facts and their applications.

I wish all of you a grand success in the ensuing Joint Entrance Examination. Your valuable suggestions and constructive criticism for the betterment of the book are welcome.

M.S. Chouhan

Preface

It is a matter of great pleasure for me to present the eleventh edition of **"Advanced Problems in Organic Chemistry for JEE"** before JEE aspirants. During my teaching experience, I felt that the facts may be made more and more clear to the students through problematic approach. Although an ocean of material in Organic Chemistry is available with the students, yet the approach to design the problems has been changed in recent years and if one tries to swim in this ocean, it will be a very difficult task. To make the students more familiar with trends and tricks how to solve problems, the present problem book has been presented. In the current scenario of stiff competition especially for JEE, one must be clear that almost all the sincere applicants are well equipped with the facts of subject, yet the winner is one who knows how to use these equipments with accuracy and efficiency. As an experienced teacher, I would like to suggest students three golden rules to score high in Organic Chemistry:

1. Don't get behind
2. Work out a number of problems of different types
3. Revise through short notes / learning chart.

I hope that the present book will cater to the needs of JEE aspirants & as a matter of fact, they will enjoy the present venture and I would feel rewarded if this book is found helpful to the students and teachers in real terms. All attempts have been made to make the book error free however a few misprints may inadvertently creep.

I acknowledge the blessing and support of my mother Smt. Raj Kanwar, father Shri B.S. Chouhan, brother Dr. V.S. Chouhan, my wife and daughter. They inspired me all the time during the preparation of this book.

The support and valuable suggestions from my colleagues especially Mr. N. Avasthi , Mr. V. K. jaiswal, Mr. Nitin Jain, Mr. N.K. Sethia, Mr. Vikash Gupta, Mr. Pankaj Joshi, Dr. S. Kothari, Mr. Vineet Khatri, Mr. Ashish Mishra, Mr. Manish Arora, Mr. Govind Khandelwal, Mr. Rahul Pareek, Mr. Rahul Malav, Mr. Divyesh Tiwari, Mr. Omkar Kelapure, Mr. Kishore Kilani, Mr. Mayank Pareek, Mr. Gurpreet Singh, Mr. Yogesh Jain, Madam Anjana Kamal , Mr. Aneet Choudhary, Mr. Shaliwahan Singh Rathore, Mr. Akshay Chaudhary, Mr. Hanuman Sahay, Mrs. Neha Joshi, Mrs. Neetu Jha, Mr. Kamlesh Gupta and Mr. Kumud Ranjan are highly acknowledged. I also pay my sincere thanks to all the esteemed members of **M/s Shri Balaji Publications** in bringing out this book in such a nice form.

In the last, constructive criticism and valuable suggestions from the readers are most welcome to make the book more useful.

M.S. CHOUHAN

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Δ
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H2,Ni
160°C
(Catalytic reduction)

LEVEL-2

1.

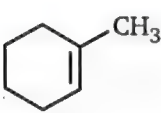
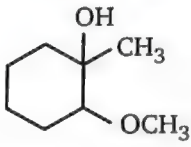
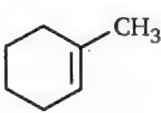
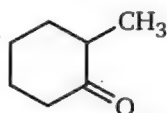
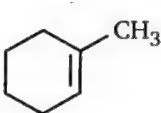
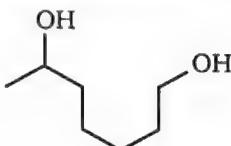
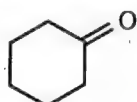
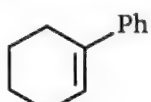
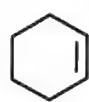
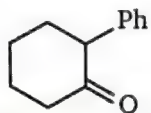
Reagents

A. HCl	B. Br_2	C. $Hg(OAc)_2$ in H_2O	D. $B_2H_6(BH_3)$ in ether
E. H_2O_2	F. $KMnO_4$ in H_2O	G. HOBr	H. $NaBH_4$

In each reagent box write a letter designating the best reagent and condition selected from the above list of reagents.

Reactant	Reagent		Product
$(CH_3)_2CHCH=CH_2$ 3-methyl-1-butene	(i)	☐	$(CH_3)_2CHCH(Cl)CH_3$ 2-Chloro-3-methyl butane
	(ii)	☐	$(CH_3)_2CHCHBrCH_2Br$ 1, 2-dibromo-3-methyl butane
	(iii)	☐	$(CH_3)_2CHCHOHCH_2Br$ 1, bromo-3-methyl 2–butanol
	(iv)	☐	$(CH_3)_2CHCH(OH)CH_3$ 3-methyl-2-butanol
	(v)	☐	$(CH_3)_2CHCH(OH)CH_2OH$ 3-methyl-1, 2-butanediol

2. **Propene ($CH_3-CH=CH_2$)** can be transformed to compounds (a to j) listed in the left-hand column.

Write letter designating the reagent, you believe will achieve desired transformation. In the case of a multi step sequence write the reagent in the order they are to be used.

	Desired Product	No. of Steps	Write options		Reagent List
a.	$CH_3CHBrCH_2Br$	one		A.	$Hg(OAc)_2$ in H_2O
b.	$(CH_3)_2CHOH$	two		B.	B_2H_6 in THF

c.	$CH_3CH_2CH_2OH$	two		C.	$NaBH_4$ in alcohol
d.	CH_3COCH_3	three		D.	Br_2 in CH_2Cl_2
e.	CH_3CH_2CHO	three		E.	H_2O_2 in aqueous base
f.	$CH_3CH(OH)CH_2Br$	one		F.	HOBr (NBS in aqueous acetone)
g.	$(CH_3)_2CHBr$	one		G.	HBr in CH_2Cl_2
h, k.	$CH_3CH(OH)\ CH_2OH$	two		H.	OsO_4 in ether
i.	$CH_3-CH_2-CH_2-Cl$	three		I.	Thionyl chloride ($SOCl_2$)
j.	$CH_3-C\equiv CH$	two		J.	$NaHSO_3$ in aqueous acetone
				K.	NaOH in alcohol and reflux
				L.	$NaNH_2$ (strong base)

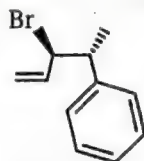
3. In each reaction box write a single letter designating the best reagent and condition selected from the list at bottom of the page.

(F.S., → first step, S.S → second step, T.S. → third step)

Reaction	Reactant	Options	Product
1.	1-methylcyclohexene (CH_3)	F.S. ☐ S.S. ☐ →	OH, CH_3, OCH_3
2.	1-methylcyclohexene (CH_3)	F.S. ☐ S.S. ☐ T.S. ☐ →	CH_3, O
3.	1-methylcyclohexene (CH_3)	F.S. ☐ S.S. ☐ →	OH, OH
4.	cyclohexanone (O)	F.S. ☐ S.S. ☐ →	Ph
5.	cyclohexene	F.S. ☐ S.S. ☐ T.S. ☐ →	Ph, O

A. $NaBH_4$/alcohol	**B.** $Ph-CO_3H/CH_2Cl_2$	**C.** PCC	**D.** CH_3ONa/CH_3OH
E. B_2H_6 in THF	**F.** H_2O_2/aq. NaOH	**G.** H_3PO_4 & heat	**H.** $AlCl_3/C_6H_6$
I. O_3 in CH_2Cl_2	**J.** Br_2 in CH_2Cl_2	**K.** 20% KOH & heat	**L.** Ph – Li/ether

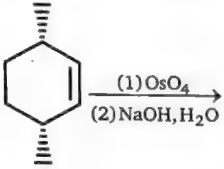
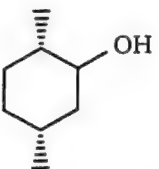
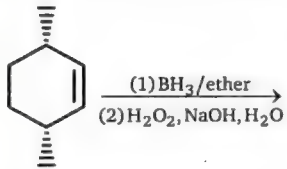
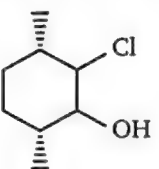
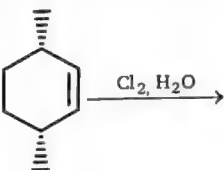
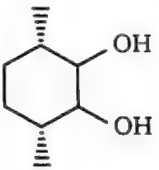
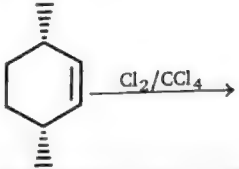
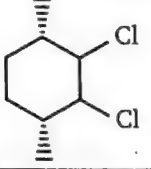
4. Match the reagents a-j with products A-J. There is one best product for each reaction.

Br

(x)

The molecule (x) is the starting material for all reactions in problem. Do the ones you know first and then tackle the rest by deductive reasoning

Products: A, B, C, D, E, F, G, H, I, J

	Reagents	Option
(a)	H_2O heat, pH 7	
(b)	$F_3C-C(=O)-O-OH$	
(c)	tBuOK, polar aprotic solvent	
(d)	(1) O_3, ether (2) H_2O, NaOH, H_2O_2	
(e)	Br_2, CCl_4	
(f)	NBS, hν, CCl_4	
(g)	(1) $H_3O(+)$ (2) NaOH, H_2O	
(h)	(1) BH_3, ether (2) H_2O_2	
(i)	(1) OsO_4 (2) NaOH, H_2O	
(j)	H_2/Pd/C(EtOH)	

5. Match the column:

	Column (I)		Column (II)
(a)	$CH_3—C\equiv C—CH_3$	**(p)**	*cis*-product with H_2/ Pd - $BaSO_4$
(b)	$CH_3—CH_2—C\equiv CH$	**(q)**	*Trans*-product with Na/ liq. NH_3
(c)	$CH_3—C\equiv CH$	**(r)**	White with amm. $AgNO_3$
(d)	$CH_3—C\equiv C—Et$	**(s)**	H_2 gas with Na

6. Match the column I with column II and with column III (Matrix).

Column-I		Column- II		Column- III	
Reaction		Nature of product formed		Number of chiral center present in product. (Consider only one isomer in case of racemic mixture or Diastereomer)	
(a)	H, CH_3 $\xrightarrow[CCl_4]{Br_2}$	**(p)**	Racemic mixture	**(w)**	0
(b)	H, CH_3 $\xrightarrow[CCl_4]{Br_2}$	**(q)**	Meso	**(x)**	1
(c)	CH_3 $\xrightarrow[CCl_4]{Br_2}$	**(r)**	Diastereomer	**(y)**	2
(d)	$CH_3(H)C=C(H)CH_3$ $\xrightarrow[CCl_4]{Br_2}$	**(s)**	Vicinal dihalide	**(z)**	3

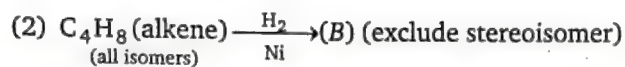
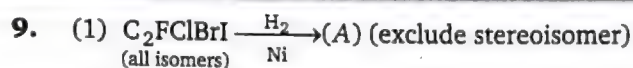
7. Match the column I and II.

Column (I)		Column (II)	
	Reaction		**Product**
(a)	$\xrightarrow[(2)\,NaOH,\,H_2O]{(1)\,OsO_4}$	**(p)**	OH
(b)	$\xrightarrow[(2)\,H_2O_2,\,NaOH,\,H_2O]{(1)\,BH_3/ether}$	**(q)**	Cl, OH
(c)	$\xrightarrow{Cl_2,\,H_2O}$	**(r)**	OH, OH
(d)	$\xrightarrow{Cl_2/CCl_4}$	**(s)**	Cl, Cl

8.

Sum of molecular mass of A, B, C, D (i.e. $A + B + C + D$) is equal to :	

9. (1) $C_2FClBrI \xrightarrow[Ni]{H_2} (A)$ (exclude stereoisomer)
(all isomers)

(2) C_4H_8 (alkene) $\xrightarrow[Ni]{H_2} (B)$ (exclude stereoisomer)
(all isomers)

Total number of products *A* and *B* (i.e. *A* + *B*) is equal to :	

10.

Reaction 1	**Reaction 2**
CH_3; H—C—Br; CH ‖ CH (*cis*) $\xrightarrow[CCl_4]{Br_2}$ (*P*); H—C—Br; CH_3	CH_3; H—C—Br; CH ‖ CH (*trans*) $\xrightarrow[CCl_4]{Br_2}$ (*Q*); H—C—Br; CH_3
Reaction 3	**Reaction 4**
CH_3; H—C—Br; CH ‖ CH (*cis*) $\xrightarrow[CCl_4]{Br_2}$ (*R*); CH_3	CH_3; H—C—Br; CH ‖ CH (*trans*) $\xrightarrow[CCl_4]{Br_2}$ (S); CH_3

Sum of products *P*, *Q*, *R*, *S* (i.e. *P* + *Q* + *R* + *S*) is equal to :	

11. Comprehension

Vladimir Markovnikov rule :

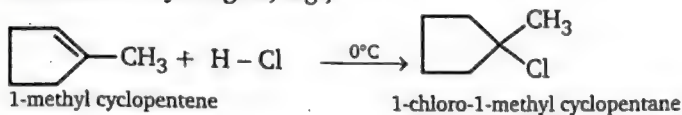
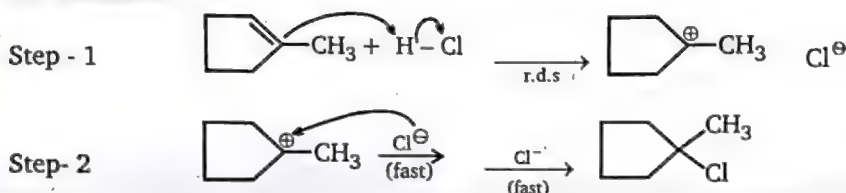
Alkenes undergo electrophilic addition reactions. It is triggered by the acid acting as a electrophile toward π-electrons of the double bond.

Markovnikov's rule states that when an unsymmetrically substituted alkene reacts with a hydrogen halide, the hydrogen atom adds to the carbon that has the greater number of hydrogen, e.g.,

1-methyl cyclopentene $-CH_3 + H-Cl \xrightarrow{0°C}$ 1-chloro-1-methyl cyclopentane (CH_3, Cl)

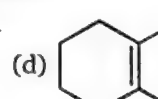
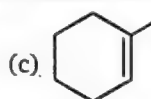
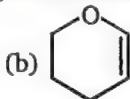
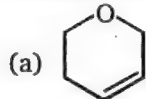
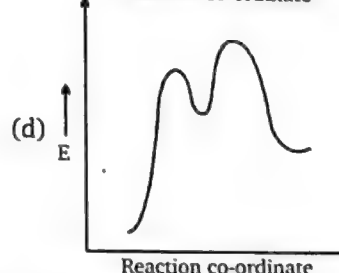
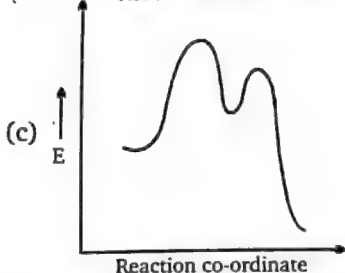
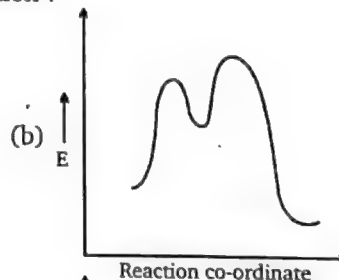
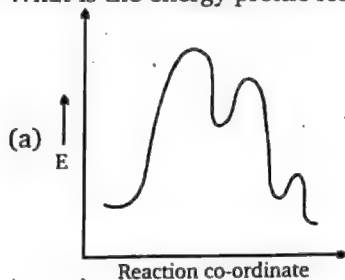
Mechanism :

Step - 1 $\quad -CH_3 + H-Cl \xrightarrow[\text{r.d.s}]{} \overset{\oplus}{}-CH_3 \quad Cl^{\ominus}$

Step- 2 $\quad \overset{\oplus}{}-CH_3 \xrightarrow[\text{(fast)}]{Cl^{\ominus}} \quad \xrightarrow[\text{(fast)}]{Cl^{-}}$ (CH_3, Cl)

A. Which of the following is most reactive toward Markovnikov addition ?

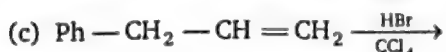
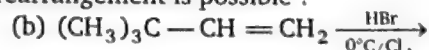
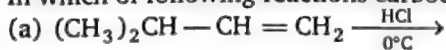
(a)

(b)

(c)
(d)

B. What is the energy profile for the given reaction ?

C. In which of following reactions carbocation rearrangement is possible ?

(a) $(CH_3)_2CH-CH=CH_2 \xrightarrow[0°C]{HCl}$

(b) $(CH_3)_3C-CH=CH_2 \xrightarrow[0°C/CCl_4]{HBr}$

(c) $Ph-CH_2-CH=CH_2 \xrightarrow[CCl_4]{HBr}$

(d) All of these

D. Identify the major products r_1, r_2 and r_3 in the given reactions.

1-Methylcyclohexene $\xrightarrow[H_2O]{HBr}$ r_1

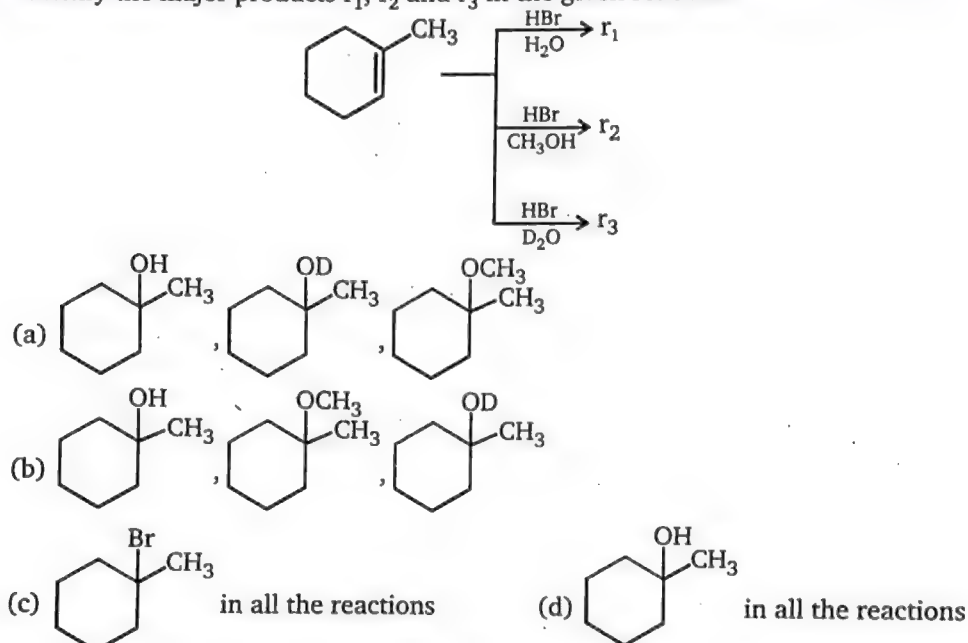
$\xrightarrow[CH_3OH]{HBr}$ r_2

$\xrightarrow[D_2O]{HBr}$ r_3

(a) 1-methylcyclohexanol (OH, CH_3), 1-methylcyclohexyl OD (OD, CH_3), 1-methoxy-1-methylcyclohexane (OCH_3, CH_3)

(b) 1-methylcyclohexanol (OH, CH_3), 1-methoxy-1-methylcyclohexane (OCH_3, CH_3), 1-methylcyclohexyl OD (OD, CH_3)

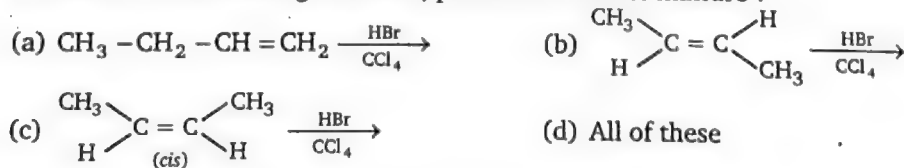
(c) 1-bromo-1-methylcyclohexane (Br, CH_3) in all the reactions

(d) 1-methylcyclohexanol (OH, CH_3) in all the reactions

E. In which of the following reactions, product is racemic mixture ?

(a) $CH_3-CH_2-CH=CH_2 \xrightarrow[CCl_4]{HBr}$

(b) $(CH_3)(H)C=C(H)(CH_3)$ (trans) $\xrightarrow[CCl_4]{HBr}$

(c) $(CH_3)(H)C=C(CH_3)(H)$ (*cis*) $\xrightarrow[CCl_4]{HBr}$

(d) All of these

F. In which of the following reactions, diastereomers will be formed ?

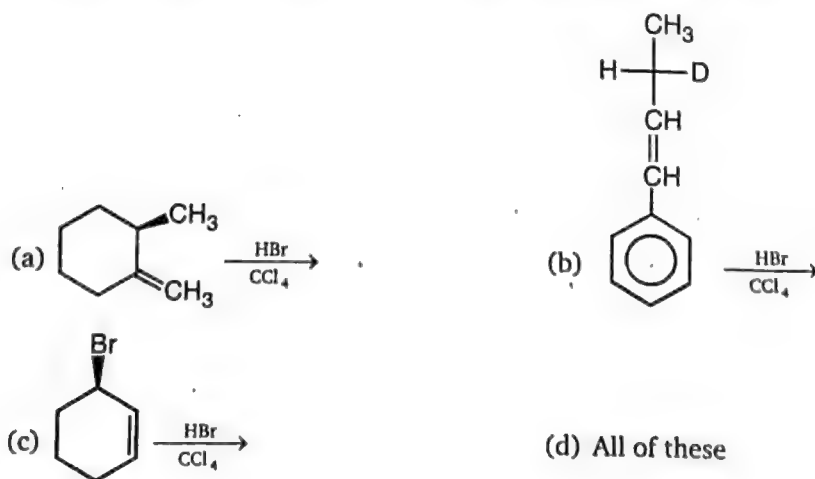
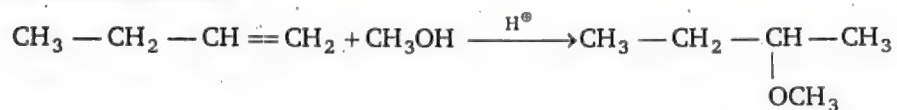
(a) 1,2-dimethylcyclohexene derivative (CH_3, CH_3) $\xrightarrow[CCl_4]{HBr}$

(b) $CH_3-C(H)(D)-CH=CH-C_6H_5$ $\xrightarrow[CCl_4]{HBr}$

(c) 3-bromocyclohexene (Br) $\xrightarrow[CCl_4]{HBr}$

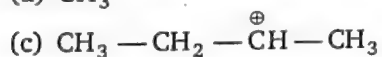
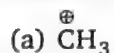
(d) All of these

12. Comprehension

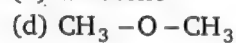
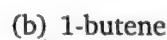
$$CH_3-CH_2-CH=CH_2+CH_3OH \xrightarrow{H^{\oplus}} CH_3-CH_2-\underset{\displaystyle OCH_3}{\underset{|}{CH}}-CH_3$$

Consider the above reaction and answer A to E.

A. What is electrophile in first step ?

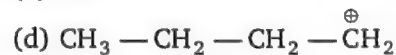
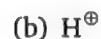
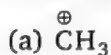
(a) $\overset{\oplus}{C}H_3$ (b) $H^{\oplus}$

(c) $CH_3-CH_2-\overset{\oplus}{C}H-CH_3$ (d) $HO^{\oplus}$

B. What is nucleophile in first step ?

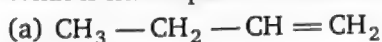
(a) CH_3OH (b) 1-butene

(c) H_2O (d) CH_3-O-CH_3

C. What is electrophile in second step ?

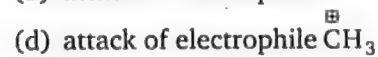
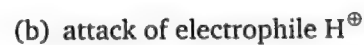
(a) $\overset{\oplus}{C}H_3$ (b) $H^{\oplus}$

(c) $CH_3-CH_2-\overset{\oplus}{C}H-CH_3$ (d) $CH_3-CH_2-CH_2-\overset{\oplus}{C}H_2$

D. What is nucleophile in second step ?

(a) $CH_3-CH_2-CH=CH_2$ (b) CH_3OH

(c) H_2O (d) CH_3-O-CH_3

E. Which step is rate determining step ?

(a) attack of nucleophile CH_3OH (b) attack of electrophile $H^{\oplus}$

(c) attack of nucleophile H_2O (d) attack of electrophile $\overset{\oplus}{C}H_3$

13. Match the column I and II :

	Column (I)		Column (II)
	Conversion		**Reagent**
(a)	(CH_3-phenyl-cyclopentyl) ⟶ (CH_2–Br phenyl, Br on cyclopentyl)	**(p)**	SO_2Cl_2 / $h\nu$ (2 equivalent)
(b)	(CH_3-phenyl-cyclopentyl) ⟶ (CH_2– Cl phenyl, Cl on cyclopentyl)	**(q)**	NBS (2 equivalent)
(c)	(CH_3-phenyl-cyclopentyl) ⟶ (CH_2–Br phenyl, Cl on cyclopentyl)	**(r)**	NBS then SO_2Cl_2/$h\nu$
(d)	(CH_3-phenyl-cyclopentyl) ⟶ (CH_2–Cl phenyl, Br on cyclopentyl)	**(s)**	SO_2 Cl_2 / $h\nu$ then NBS

ANSWERS — LEVEL 2

1. (i) – A; (ii) – B; (iii) – G; (iv) – C; (v) – F
2. a – D; b – A, C; c – B, E; d – A, C, F; e – B, E, F; f – F; g – G; h – I, K; i – B, E, I; j – D, L
3. Reaction 1 : B, D; Reaction 2 : E, F, C Reaction 3 : I, A
   Reaction 4 : L, G Reaction 5 : B, L, C
4. a – C; b – D; c – A; d – F; e – I; f – J; g – E; h – H; i – B; j – G
5. a – p, q; b – r, s; c – r, s; d – p, q
6. a – r, s – z; b – p, s – y; c – p, s – y; d – q, s – y
7. a – r; b – p; c – q; d – s
8. $A+B+C+D=312$
9. $A+B=5$
10. $P+Q+R+S=8$
11. A – b; B – c; C – d; D – b; E – d; F – d
12. A – b; B – b; C – c; D – b; E – b
13. a-q; b-p; c-s; d-r

4C HYDROCARBONS (ALKYNES)

LEVEL-1

1.

; Product (*B*) is :

2. (2-butene) $\xrightarrow[CCl_4]{Br_2}$ $\xrightarrow[\text{(ii) } NaNH_2]{\text{(i) alc.KOH}}$ $\underset{\text{major}}{(A)}$; Product (*A*) is :

(a) $H_2C=CH-CH=CH_2$ (b) $CH_3-C\equiv C-CH_3$

(c) $CH_3-CH_2-C\equiv CH$ (d) $CH_3-CH=C=CH_2$

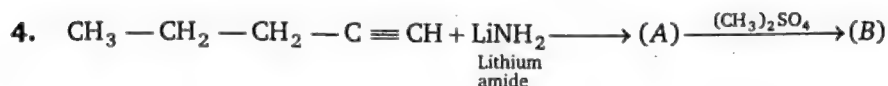
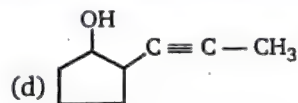
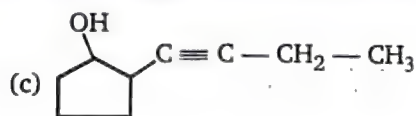
3. $CH_3CH_2C\equiv CH \xrightarrow[\text{liq. } NH_3]{NaNH_2} I \xrightarrow[Et_2O]{\text{cyclopentanone}} J \xrightarrow{H^{\oplus}} (K)$

Product (*K*) of the above reaction is :

(a) 2-($C\equiv C-Et$)cyclopentanone (b) 1-($C\equiv C-Et$)cyclopentan-1-ol (OH)

(c) (cyclopentane bearing OH and) $C \equiv C - CH_2 - CH_3$

(d) (cyclopentane bearing OH and) $C \equiv C - CH_3$

4. $CH_3 - CH_2 - CH_2 - C \equiv CH + \underset{\text{Lithium amide}}{LiNH_2} \longrightarrow (A) \xrightarrow{(CH_3)_2SO_4} (B)$

Give the structural formula of compound (*B*) :

(a) $CH_3 - (CH_2)_2 - C \equiv C - SO_3H$

(b) $CH_3 - (CH_2)_2 - C \equiv C - CH_3$

(c) $CH_3 - (CH_2)_2 - C \equiv C - CH_2 - O - \overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}} - H$

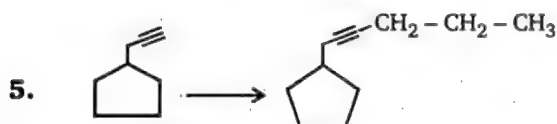
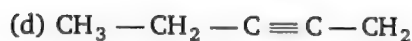
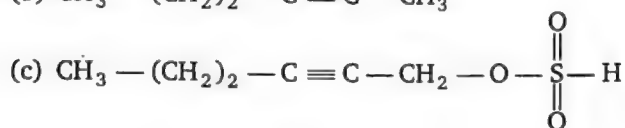
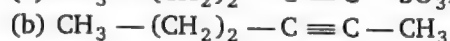
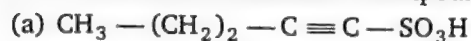
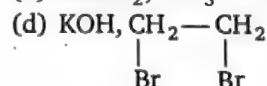
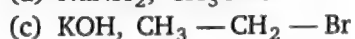
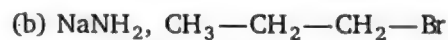
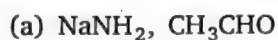
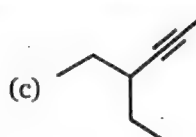
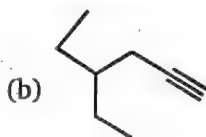
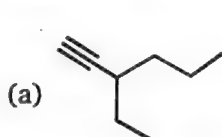
(d) $CH_3 - CH_2 - C \equiv C - CH_2$

5. (ethynylcyclopentane) $\longrightarrow$ (cyclopentyl–C≡C–$CH_2 - CH_2 - CH_3$) ; This conversion can be acheived by :

(a) $NaNH_2$, CH_3CHO

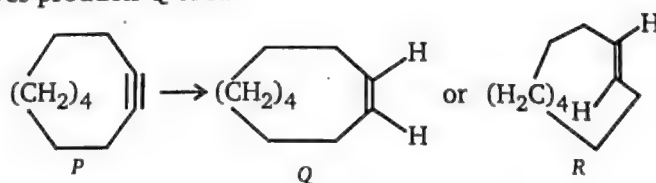
(b) $NaNH_2$, $CH_3—CH_2—CH_2—Br$

(c) KOH, $CH_3 - CH_2 - Br$

(d) KOH, $\underset{Br}{CH_2} — \underset{Br}{CH_2}$

6. Which alkyne will give 3-ethylhexane on catalytic hydrogenation ?

(a) (b) (c) (d) All of these

7. Reactant *P* gives products *Q* or *R*.

$(CH_2)_4$ (cyclic alkyne) $\longrightarrow$ $(CH_2)_4$ (cis alkene, H, H) or $(H_2C)_4$ (trans alkene, H, H)

P *Q* *R*

The possible reagents are :

(I) $2Na/liq. NH_3$ (II) $H_2/Pd/CaCO_3$(quinoline) (III) $2H_2/Pd/C$

The correct statement with respect to the above conversion is/are :

(a) *Q* is obtained on treatment with reagent (I)

(b) *R* and *Q* are obtained on treatment with reagent (II)

(c) *R* is obtained on treatment with reagent (I)

(d) R is obtained on treatment with reagent (II)

8. $Br-(CH_2)_{12}-C\equiv CH \xrightarrow{NaNH_2} (A) \xrightarrow[\text{Catalyst}]{\text{Lindlar}} (B)$; Product (B) is :

(a)

(b)

(c)

(d) $Br-(CH_2)-CH=CH_2$

9. $Ph-C\equiv CH \xrightarrow[\text{MeOH}]{\text{MeO}^-}$ Major product of the reaction is :

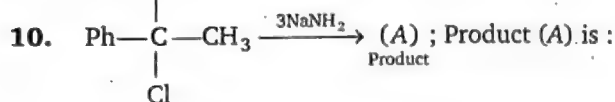
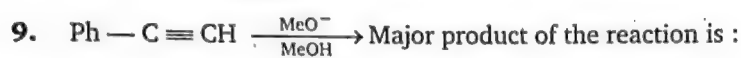
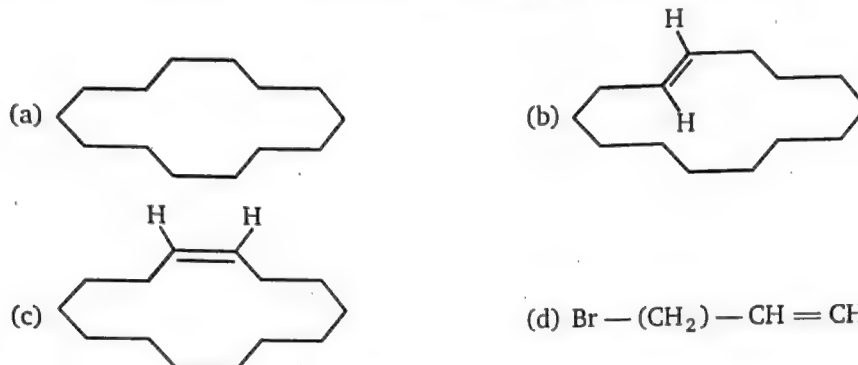
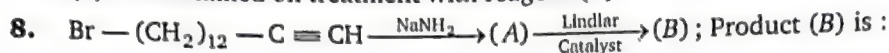
(a) $(Ph)(H)C=C(H)(H)$

(b) $(Ph)(H)C=C(OMe)(H)$

(c) $Ph-C\equiv C-OMe$

(d) $Ph-C(OMe)=CH_2$

10. $Ph-C(Cl)_2-CH_3 \xrightarrow[\text{Product}]{3NaNH_2} (A)$; Product (A) is :

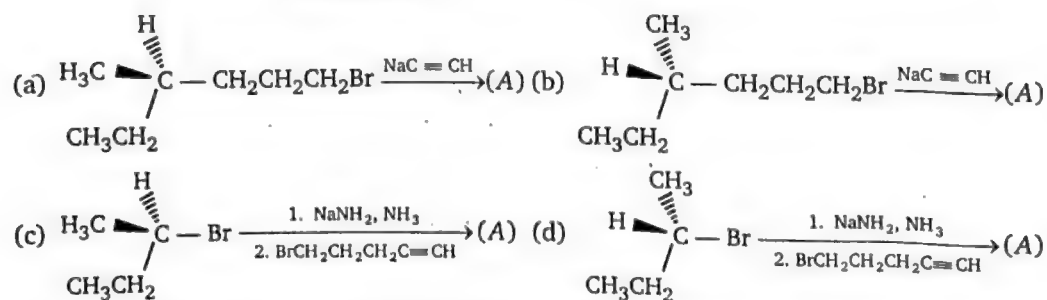
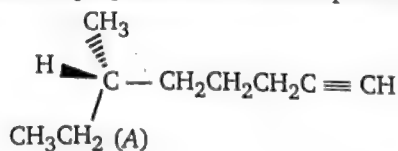
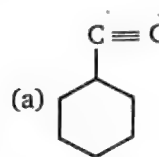
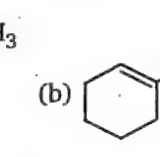
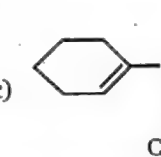
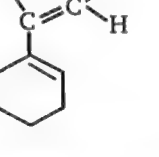
(a) $Ph-CH=CH_2$ (b) $Ph-C\equiv CH$ (c) $Ph-CH_2-CH_3$ (d) $Ph-C\equiv C^{\ominus}Na^{\oplus}$

11. Which combination is best for preparation of the compound (A) shown below ?

$$(CH_3)(H)(CH_3CH_2)C-CH_2CH_2CH_2C\equiv CH \quad (A)$$

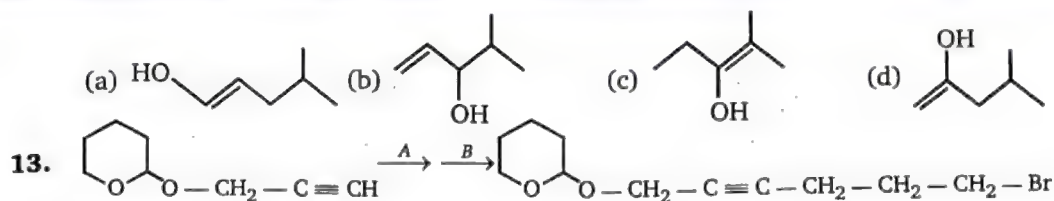
(a) $(H)(H_3C)(CH_3CH_2)C-CH_2CH_2CH_2Br \xrightarrow{NaC\equiv CH} (A)$

(b) $(CH_3)(H)(CH_3CH_2)C-CH_2CH_2CH_2Br \xrightarrow{NaC\equiv CH} (A)$

(c) $(H)(H_3C)(CH_3CH_2)C-Br \xrightarrow[\text{2. } BrCH_2CH_2CH_2C\equiv CH]{\text{1. } NaNH_2,\ NH_3} (A)$

(d) $(CH_3)(H)(CH_3CH_2)C-Br \xrightarrow[\text{2. } BrCH_2CH_2CH_2C\equiv CH]{\text{1. } NaNH_2,\ NH_3} (A)$

12. Which one of the following is the intermediate in the preparation of a ketone by hydration of an alkyne in the presence of sulfuric acid and mercury (II) sulphate ?

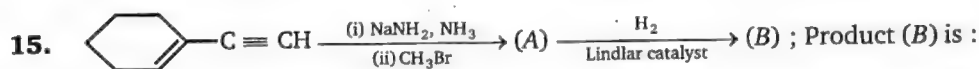
(a) HO (b) OH (c) OH (d) OH

13. THP–O — CH_2 — C ≡ CH $\xrightarrow{A}$ $\xrightarrow{B}$ THP–O — CH_2 — C ≡ C — CH_2 — CH_2 — CH_2 — Br

To carry out above conversion, (*A*) and (*B*) respectively, are :

(a) $NaNH_2$, Cl — CH_2 — CH_2 — CH_2 — Br
(b) $NaNH_2$, F — CH_2 — CH_2 — CH_2 — Br
(c) $NaNH_2$, I — CH_2 — CH_2 — CH_2 — Br
(d) $NaNH_2$, I — CH_2 — CH_2 — CH_2 — I

14. H — C ≡ C — Ph $\xrightarrow[\text{H-N(morpholine)O}]{I_2}$ Product; Product obtained in this reaction is :

(a) Ph — C(I) = CH — I (b) Ph — CH(I) — CH_2 — I
(c) Ph — C ≡ C — I (d) I — C ≡ C — H

15. (cyclohexenyl)—C ≡ CH $\xrightarrow[\text{(ii) } CH_3Br]{\text{(i) } NaNH_2, NH_3}$ (*A*) $\xrightarrow[\text{Lindlar catalyst}]{H_2}$ (*B*) ; Product (*B*) is :

16. Which of the following alkyne on treatment with H_2 (2 mole)/ Pt gives an optically inactive compound ?

(a) 3-Methyl-1-pentyne (b) 4-Methyl-1-hexyne
(c) 3-Methyl-1-heptyne (d) None of the above

17. CaC_2 (Calcium carbide) $\xrightarrow{H_2O}$ (*A*) $\xrightarrow{\text{Red hot Cu tube}}$ (*B*), Product (*B*) of the reaction is :

(a) Toluene (b) Ethyl-benzene (c) Benzene (d) Butyne

18. What is the final product, *C*, of the following reaction sequence ?

$$\text{—≡—H} \xrightarrow[\text{2. } CH_3CH_2Br]{\text{1. } NaNH_2} A$$

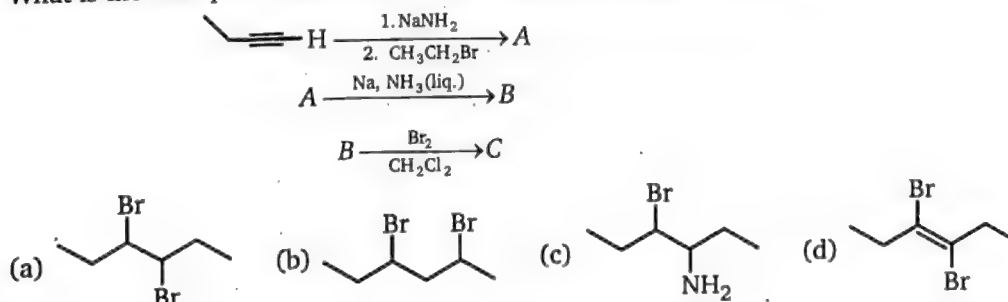
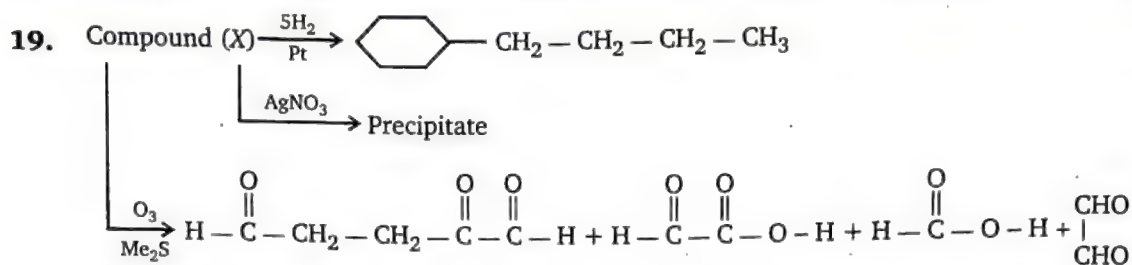
$$A \xrightarrow{Na, NH_3(liq.)} B$$

$$B \xrightarrow[CH_2Cl_2]{Br_2} C$$

(a) Br, Br (b) Br Br (c) Br, NH_2 (d) Br, Br

19. Compound (X) $\xrightarrow[Pt]{5H_2}$ (cyclohexyl)$-CH_2-CH_2-CH_2-CH_3$

Compound (X) $\xrightarrow{AgNO_3}$ Precipitate

Compound (X) $\xrightarrow[Me_2S]{O_3}$ $H-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-O-H + H-\overset{O}{\overset{\|}{C}}-O-H + \begin{matrix}CHO\\|\\CHO\end{matrix}$

Compound (X) will be :

(a) (ring)$-CH=CH-C\equiv CH$ (b) (ring)$=CH-CH_2-C\equiv CH$

(c) (ring)$=CH-CH_2-C\equiv CH$ (d) (ring)$=C=CH-C\equiv CH$

20. Choose the sequence of steps that describes the best synthesis of 1-butene from ethanol :

(a) (1) $NaC\equiv CH$; (2) H_2, Lindlar Pd

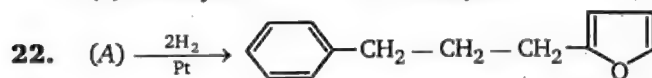
(b) (1) $NaC\equiv CH$; (2) Na, NH_3

(c) (1) HBr, heat ; (2) $NaC\equiv CH$; (3) H_2, Lindlar Pd

(d) (1) HBr, heat ; (2) $KOC(CH_3)_3$, DMSO ; (3) $NaC\equiv CH$; (4) H_2, Lindlar catalyst

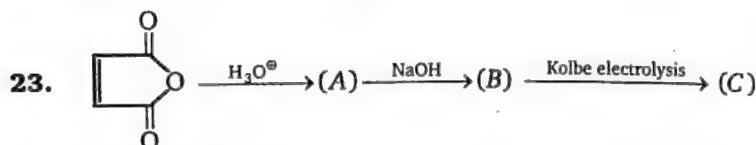
21. Which alkyne yields butanoic acid ($CH_3CH_2CH_2CO_2H$) as the only organic product on treatment with ozone followed by the hydrolysis ?

(a) 1-Butyne (b) 4-Octyne (c) 1-Pentyne (d) 2-Hexyne

22. (A) $\xrightarrow[Pt]{2H_2}$ (phenyl)$-CH_2-CH_2-CH_2-$(furan)

Carlina oxide

Unit of unsaturation in compound (A) ?

(a) 7 (b) 8 (c) 9 (d) 10

23. (maleic anhydride) $\xrightarrow{H_3O^{\oplus}}$ (A) $\xrightarrow{NaOH}$ (B) $\xrightarrow{\text{Kolbe electrolysis}}$ (C)

Product (C) of above reaction is:

(a) $H_2C=CH_2$ (b) $CH_3-C\equiv C-CH_3$

(c) $HC\equiv CH$ (d) $CH_3-CH=CH-CH_3$

24. To convert 1-butyne to 1-D-butanal, one would carry out the following steps :

(I) Sodium amide, then D_2O

(II) Disiamy lborane, then hydrogen peroxide/sodium hydroxide

(III) The transformation can not be carried out with the indicated reagents.

(a) I, followed by II (b) II, followed by I (c) III (d) II

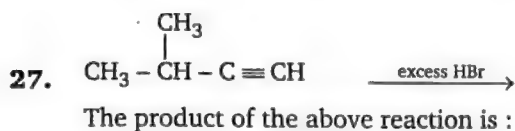
25. An unknown compound (A) has a molecular formula C_4H_6. When (A) is treated with excess of Br_2 a new substance (B) with formula $C_4H_6Br_4$ is formed. (A) forms a white ppt. with ammonical silver nitrate solution. (A) may be :

(a) But-1-yne (b) But-2-yne
(c) But-1-ene (d) But-2-ene

26. One mole of 1,2-dibromopropane on treatment with X moles of $NaNH_2$ followed by treatment with ethyl bromide gave a pentyne. The value of X is :

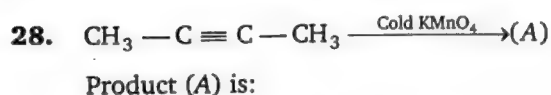
(a) One (b) Two (c) Three (d) Four

27. $CH_3-\underset{|}{\overset{CH_3}{CH}}-C\equiv CH \xrightarrow{\text{excess HBr}}$

The product of the above reaction is :

(a) $CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{Br}{\overset{|}{CH}}-\overset{Br}{\overset{|}{CH_2}}$ (b) $CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{Br}{\overset{|}{C}}=CH_2$

(c) $CH_3-\overset{CH_3}{\overset{|}{CH}}-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-CH_3$ (d) $CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{CH}}}}$

28. $CH_3-C\equiv C-CH_3 \xrightarrow{\text{Cold } KMnO_4} (A)$

Product (A) is:

(a) $CH_3-CH_2-\overset{O}{\overset{||}{C}}-\overset{O}{\overset{||}{C}}-H$ (b) $CH_3-\overset{O}{\overset{||}{C}}-\overset{O}{\overset{||}{C}}-CH_3$

(c) $CH_3-\overset{OH}{\overset{|}{CH}}-\overset{OH}{\overset{|}{CH}}-CH_3$ (d) $O=CH-CH_2-CH_2CH=O$

29. In which reaction last product is $Ph-C\equiv CH$?

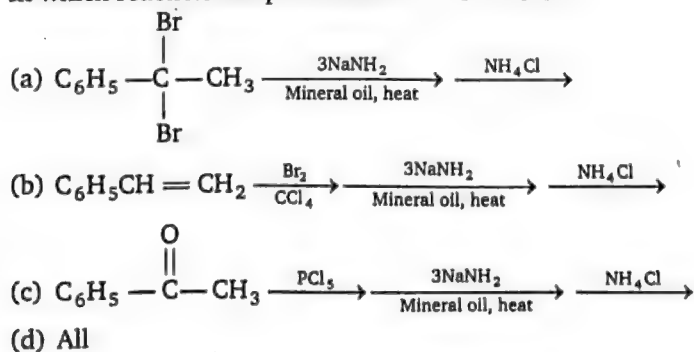
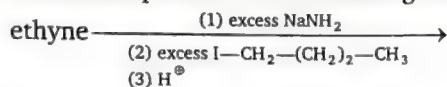
(a) $C_6H_5-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-CH_3 \xrightarrow[\text{Mineral oil, heat}]{3NaNH_2} \xrightarrow{NH_4Cl}$

(b) $C_6H_5CH=CH_2 \xrightarrow[CCl_4]{Br_2} \xrightarrow[\text{Mineral oil, heat}]{3NaNH_2} \xrightarrow{NH_4Cl}$

(c) $C_6H_5-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{PCl_5} \xrightarrow[\text{Mineral oil, heat}]{3NaNH_2} \xrightarrow{NH_4Cl}$

(d) All

30. Predict the product of the following reaction sequence.

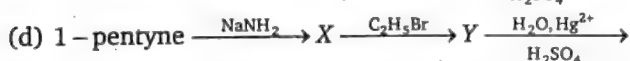
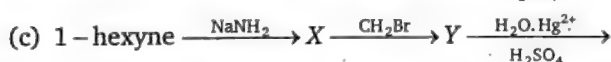
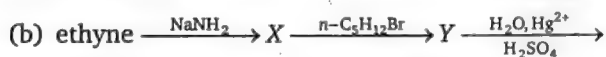
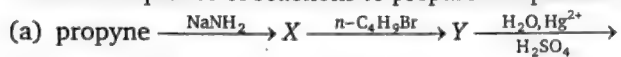
$$\text{ethyne} \xrightarrow[\substack{(2)\ \text{excess I—CH}_2\text{—(CH}_2)_2\text{—CH}_3 \\ (3)\ H^{\oplus}}]{(1)\ \text{excess NaNH}_2}$$

(a) 6-iodo-1-hexyne (b) 1-hexyne
(c) 5-decyne (d) 1-iodo-1-hexene

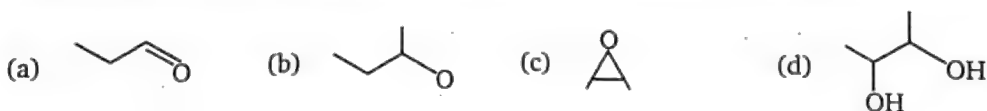
31. The best sequence of reactions to prepare 2-heptanone is

(a) propyne $\xrightarrow{NaNH_2} X \xrightarrow{n\text{-}C_4H_9Br} Y \xrightarrow[H_2SO_4]{H_2O, Hg^{2+}}$

(b) ethyne $\xrightarrow{NaNH_2} X \xrightarrow{n\text{-}C_5H_{12}Br} Y \xrightarrow[H_2SO_4]{H_2O, Hg^{2+}}$

(c) 1 – hexyne $\xrightarrow{NaNH_2} X \xrightarrow{CH_3Br} Y \xrightarrow[H_2SO_4]{H_2O. Hg^{2+}}$

(d) 1 – pentyne $\xrightarrow{NaNH_2} X \xrightarrow{C_2H_5Br} Y \xrightarrow[H_2SO_4]{H_2O, Hg^{2+}}$

32. The major product of the reaction of 2-butene with cold alkaline $KMnO_4$, is

(a) (b) (c) (d)

ANSWERS — LEVEL 1															
1.	(b)	**2.**	(b)	**3.**	(b)	**4.**	(b)	**5.**	(b)	**6.**	(d)	**7.**	(c)	**8.**	(c)
9.	(b)	**10.**	(d)	**11.**	(b)	**12.**	(d)	**13.**	(c)	**14.**	(c)	**15.**	(c)	**16.**	(a)
17.	(c)	**18.**	(a)	**19.**	(a)	**20.**	(c)	**21.**	(b)	**22.**	(c)	**23.**	(c)	**24.**	(c)
25.	(a)	**26.**	(c)	**27.**	(c)	**28.**	(b)	**29.**	(d)	**30.**	(c)	**31.**	(b)	**32.**	(d)

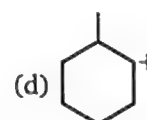
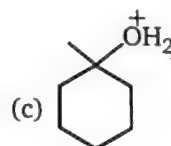
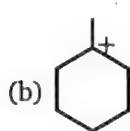
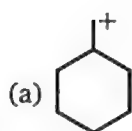
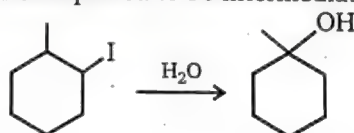
5A ALKYL HALIDES

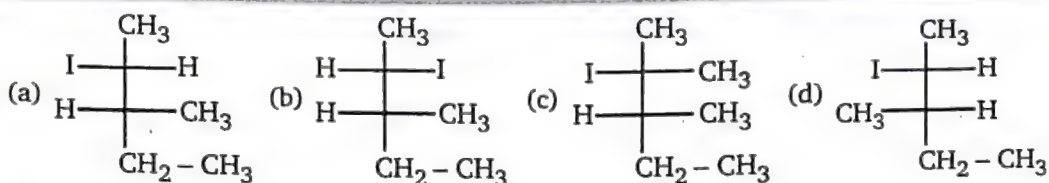
Substitution Reactions (S_{N^1}, S_{N^2}, S_{N^i})

LEVEL- 1

1. Which of the following is not expected to be intermediate of the following reaction ?

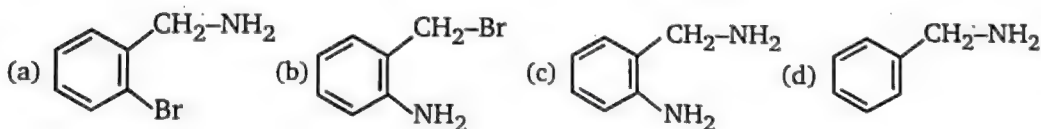
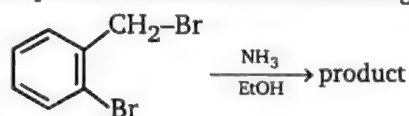
$\xrightarrow{H_2O}$ OH

(a) (b) (c) $\overset{+}{O}H_2$ (d)

2. CH_3 / Br—H / H—CH_3 / CH_2-CH_3 + NaI $\xrightarrow[\text{Acetone}]{}$ product; S_{N^2} product of the reaction is :

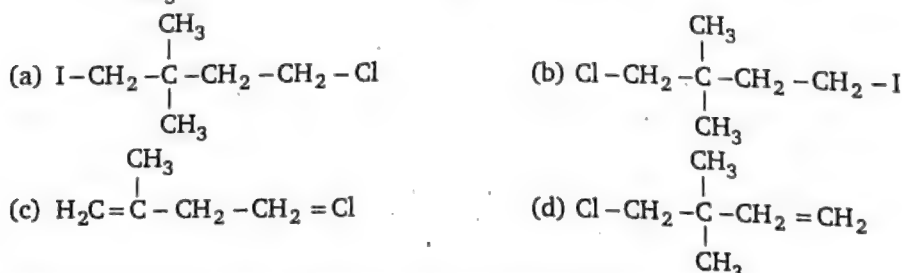
(a) Fischer projection: top CH_3; I–C–H; H–C–CH_3; bottom CH_2-CH_3
(b) Fischer projection: top CH_3; H–C–I; H–C–CH_3; bottom CH_2-CH_3
(c) Fischer projection: top CH_3; I–C–CH_3; H–C–CH_3; bottom CH_2-CH_3
(d) Fischer projection: top CH_3; I–C–H; CH_3–C–H; bottom CH_2-CH_3

3. Rate of S_{N^2} will be negligible in :

4. What is the major product obtained in the following reaction ?

(o-bromobenzyl bromide: benzene ring with CH_2-Br and Br) $\xrightarrow[EtOH]{NH_3}$ product

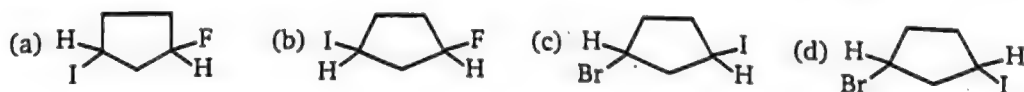
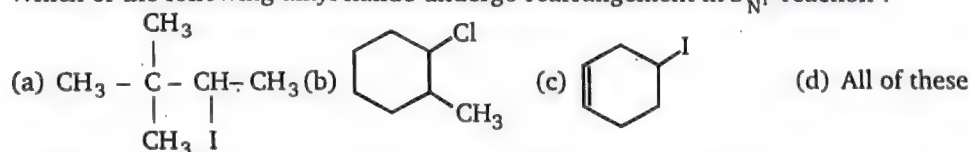
(a) benzene ring with CH_2-NH_2 and Br (b) benzene ring with CH_2-Br and NH_2 (c) benzene ring with CH_2-NH_2 and NH_2 (d) benzene ring with CH_2-NH_2

5. $Cl-CH_2-C(CH_3)_2-CH_2-CH_2-Cl + I^- \xrightarrow{DMF}$ product; Major product of this reaction is:

(a) $I-CH_2-C(CH_3)_2-CH_2-CH_2-Cl$ (b) $Cl-CH_2-C(CH_3)_2-CH_2-CH_2-I$

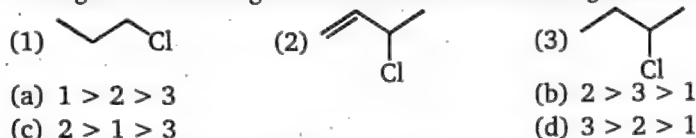
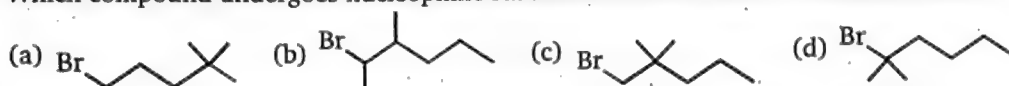
(c) $H_2C=C(CH_3)-CH_2-CH_2=Cl$ (d) $Cl-CH_2-C(CH_3)_2-CH_2=CH_2$

6. Which of the following expressions is representative of the rate law for a S_{N^2} reaction ?

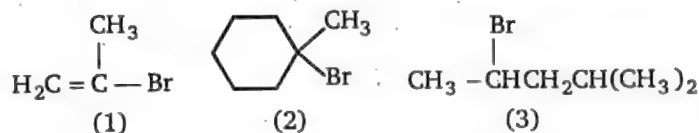
(a) Rate $= k$ [electrophile] (b) Rate $= k$ [electrophile] [nucleophile]

(c) Rate $= k$ [nucleophile]^2 (d) Rate $= k$[electrophile]^2

7. (cyclopentane with H, Br on one carbon and F, H on another) + NaI (1 mole) $\xrightarrow{Acetone}$ $\underset{(major)}{(A)}$; Major product of this reaction is :

8. Which of the following alkyl halide undergo rearrangement in S_{N^1} reaction ?

9. Arrange the following three chlorides in decreasing order towards S_{N^1} reactivity.

(1) Cl (2) Cl (3) Cl

(a) $1 > 2 > 3$ (b) $2 > 3 > 1$
(c) $2 > 1 > 3$ (d) $3 > 2 > 1$

10. Which compound undergoes nucleophilic substitution with NaCN at the fastest rate ?

11. Rank the following in order of decreasing rate of solvolysis with aqueous ethanol (fastest → slowest)

(a) $2 > 1 > 3$ (b) $1 > 2 > 3$
(c) $2 > 3 > 1$ (4) $1 > 3 > 2$

12. The reaction of 4-bromobenzyl chloride with sodium cyanide in ethanol leads to the formation of :

(a) 4-bromobenzyl cyanide (b) 4-cyanobenzyl chloride
(c) 4-cyanobenzyl cyanide (d) 4-bromo-2-cyanobenzyl chloride

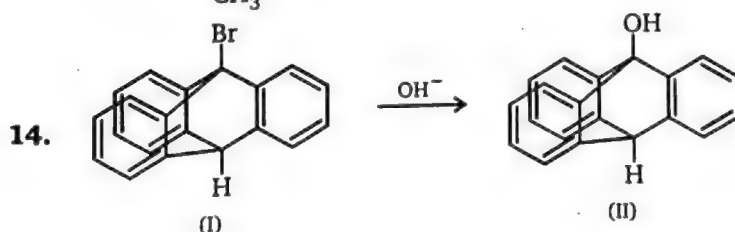
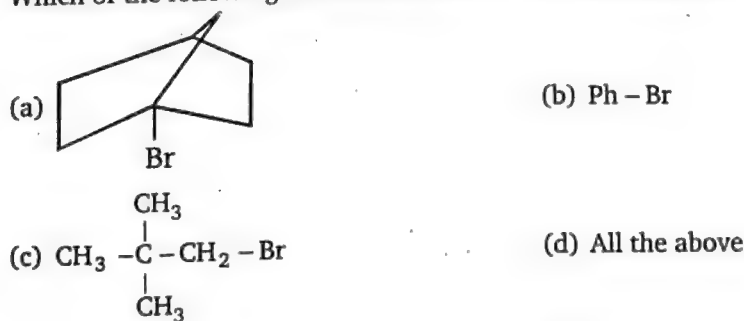
13. Which of the following reactant will not favour nucleophilic substitution reaction ?

(a)

(b) Ph – Br

(c) $CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - CH_2 - Br$

(d) All the above

14.

Conversion of I to II :

(a) takes place by S_{N^1} (b) takes place by S_{N^2}

(c) takes place both by S_{N^1} and S_{N^2} (d) does not take place

15. Which is the correct reaction coordinate diagram for the following solvolysis reaction ?

(a)

(b)

(c)

(d)

16.

product; Product of this reaction is :

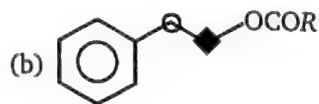
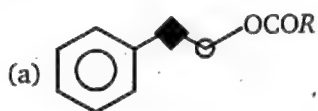
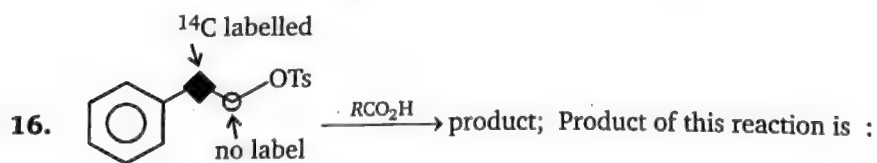
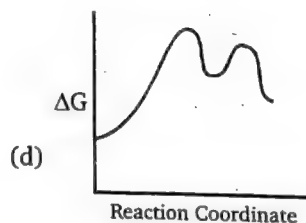
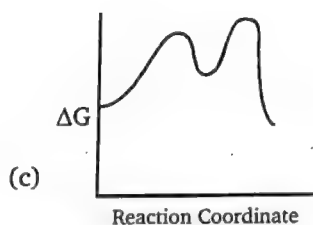
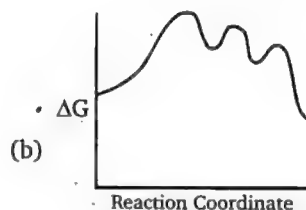
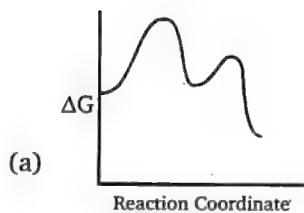
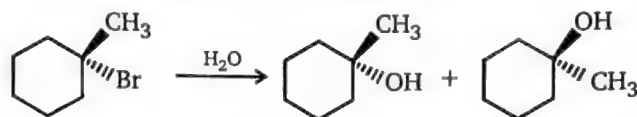
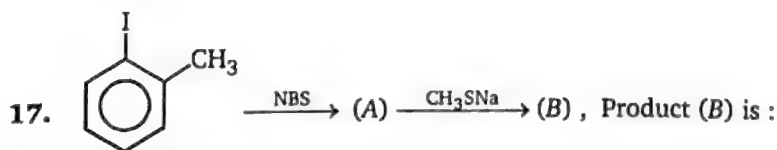
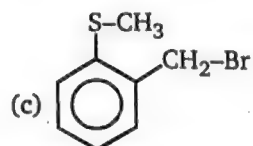
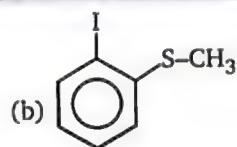
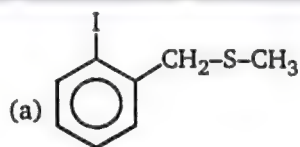
(a) (b)

(c) both (a) and (b) (d) None of these

17. [o-iodotoluene: I, CH_3] $\xrightarrow{NBS}$ (A) $\xrightarrow{CH_3SNa}$ (B) , Product (B) is :

(a) I, CH_2-S-CH_3

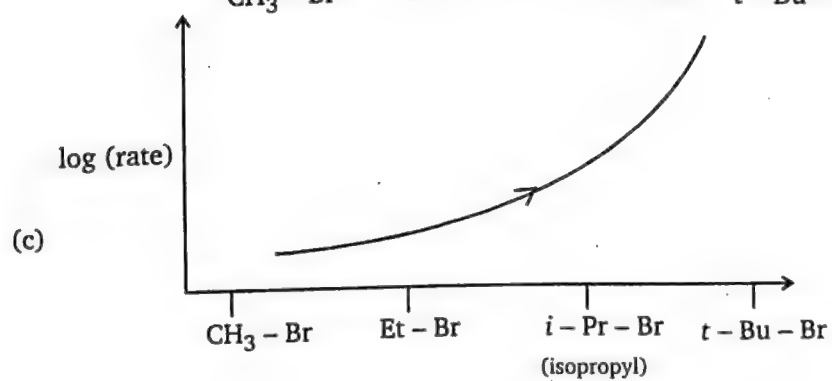
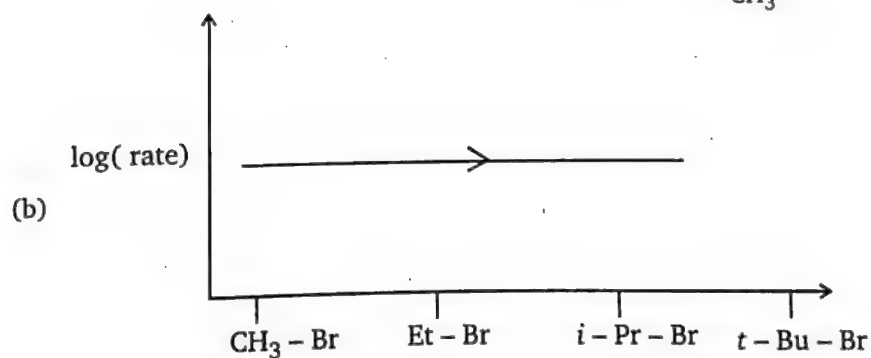
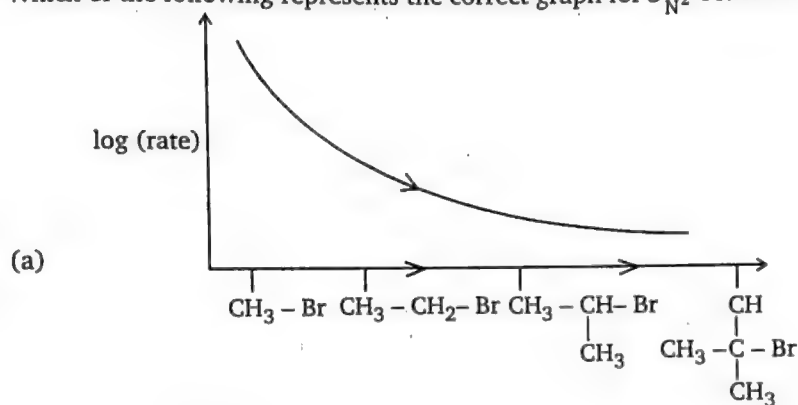
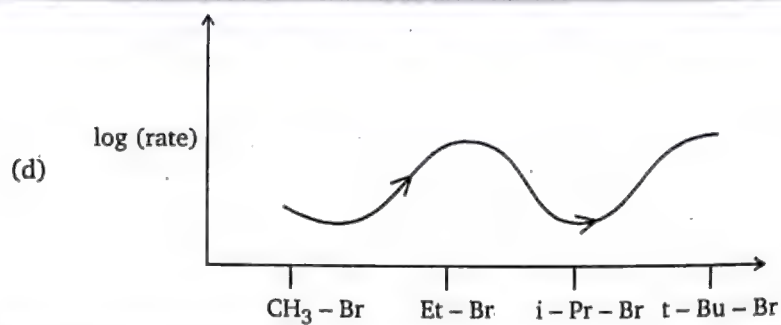
(b) I, $S-CH_3$

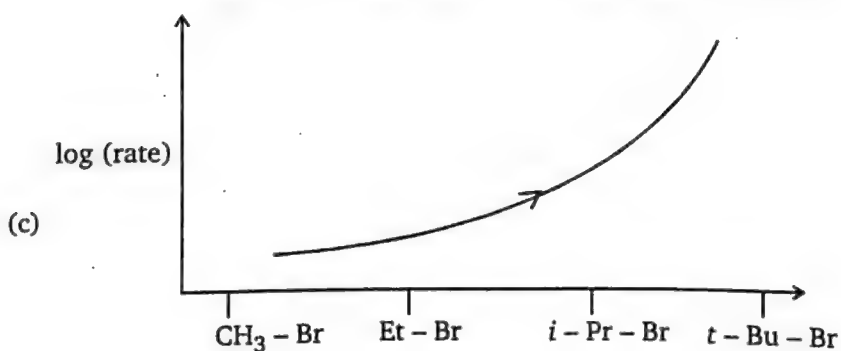
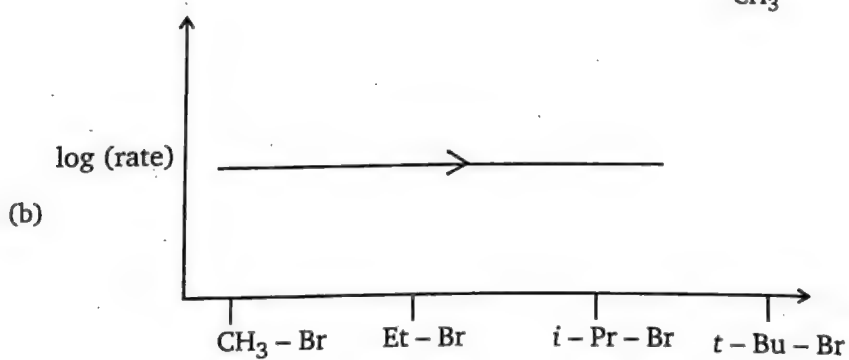
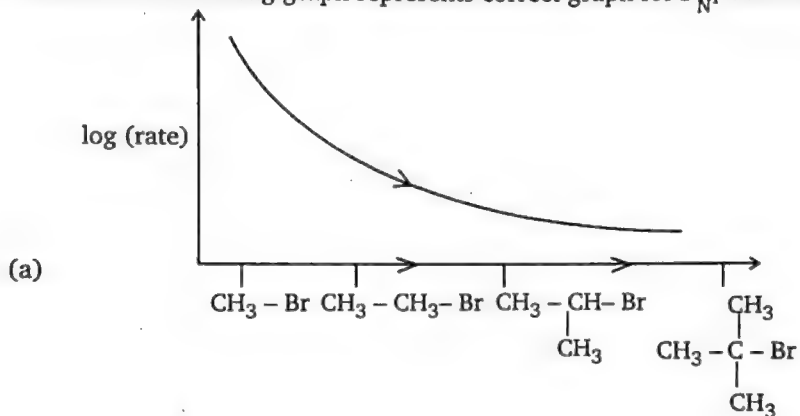
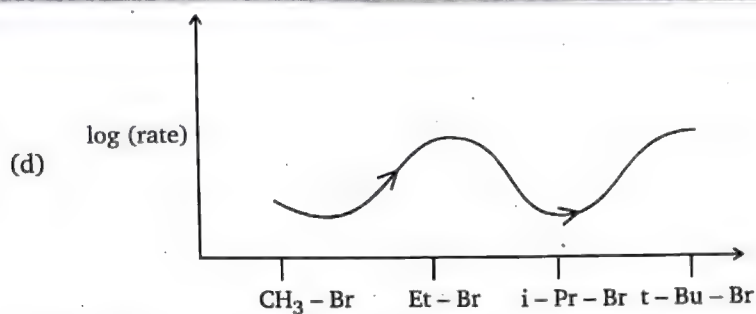
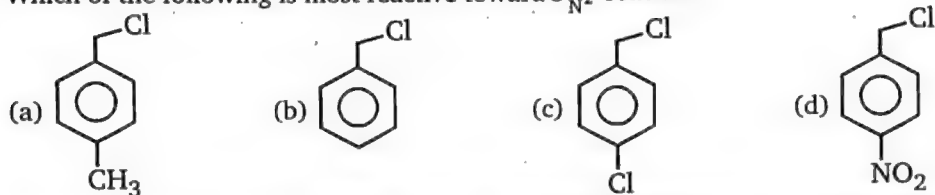
(c) $S-CH_3$, CH_2-Br

(d) None of these

18. Which of the following represents the correct graph for S_{N^2} reaction ?

(a)

(b)

(c)

19. Which of the following graph represents correct graph for S_{N^1} reaction :

(d)

20. Which of the following is most reactive toward S_{N^2} reaction ?

21. Among the given pairs, in which pair first compound reacts faster than second compound in S_{N^1} reaction ?

(a) $CH_3-CH_2-CH_2-CH_2-Br$ or $CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3$

(b) $CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2$ or $CH_3-\underset{\underset{Br}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3$

(c) [bromocyclohexane] or [3-bromocyclohexene]

(d) $CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$ or $CH_3-\underset{\underset{I}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

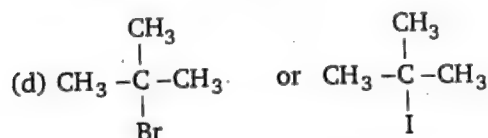
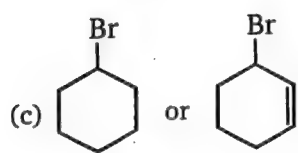
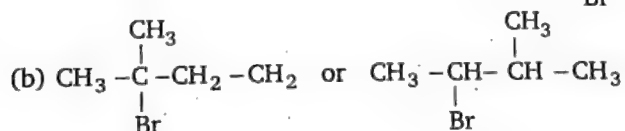
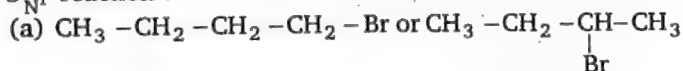
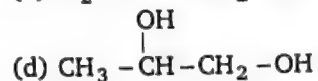
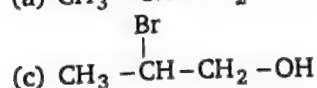
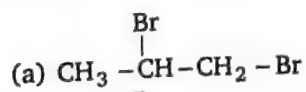
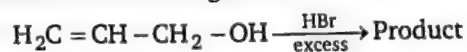
22. What is the major product of the following reaction ?

$$H_2C=CH-CH_2-OH \xrightarrow[\text{excess}]{HBr} \text{Product}$$

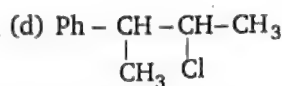
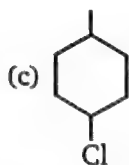
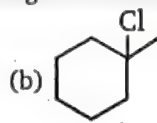
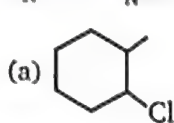
(a) $CH_3-\overset{\overset{Br}{|}}{CH}-CH_2-Br$

(b) $H_2C=CH-CH_2-Br$

(c) $CH_3-\overset{\overset{Br}{|}}{CH}-CH_2-OH$

(d) $CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-OH$

23. S_{N^1} and S_{N^2} products are same with (excluding stereoisomer) :

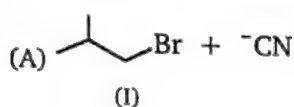
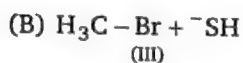
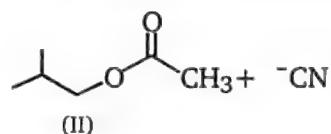
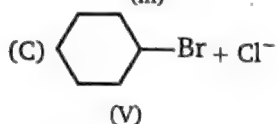
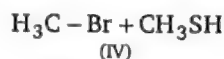
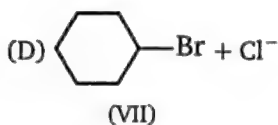
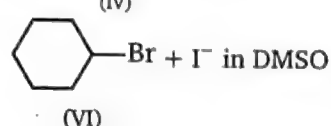
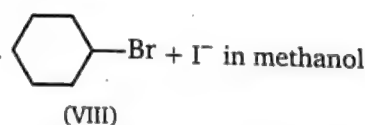
(a) Cl (b) Cl

(c) Cl (d) $Ph-\underset{CH_3}{CH}-\underset{Cl}{CH}-CH_3$

24. Consider the nucleophilic attacks given below. Select in each pair that shows the greater S_{N^2} reaction rate.

(A) Br + ^-CN (I) or CH_3 + ^-CN (II)

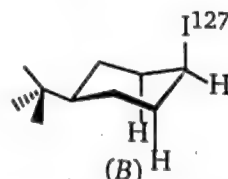
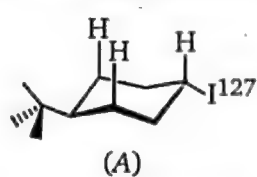
(B) $H_3C-Br + {}^-SH$ (III) or $H_3C-Br + CH_3SH$ (IV)

(C) Br + Cl^- (V) or Br + I^- in DMSO (VI)

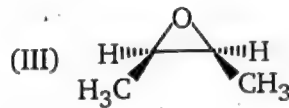
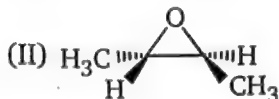
(D) Br + Cl^- (VII) or Br + I^- in methanol (VIII)

	A	B	C	D
(a)	(I) ;	(IV) ;	(VI) ;	(VIII)
(b)	(II) ;	(III) ;	(V) ;	(VIII)
(c)	(I) ;	(III) ;	(V) ;	(VIII)
(d)	(I) ;	(III) ;	(V) ;	(VII)

25. Which of the two stereoisomers of 4-t-butylcyclohexyl iodide ($^{127}I^-$) will undergo S_{N^2} substitution with $^{128}I^-$ faster, and why ?

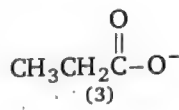
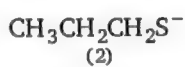
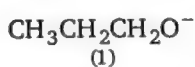
(A)

(B)

(a) *A* will react faster because it is the more stable of the two isomers
(b) *A* will react faster because it will yield a more stable product, and the transition state for both reactions is of the same energy
(c) *A* will react faster because the approach of $^{128}I^-$ can depart unhindered.
(d) *B* will react faster because it is less stable than *A*, and the transition state for both reactions is of the same energy

26. (Z)-2-Butene reacts with Br_2/H_2O. The resulting bromohydrin when treated with methoxide in methanol undergoes an intramolecular S_{N2} reaction. Taking into consideration the stereochemical consequences of the reaction mechanism involved, choose the final product(s) of these transformations.

(I) (II) (III)

(a) (I) only
(b) (II) only
(c) (III) only
(d) Equal amounts of (I) and (II)

27. Rank the following species in order of decreasing nucleophilicity in a polar protic solvent (most → least nucleophilic):

$CH_3CH_2CH_2O^-$ (1) $CH_3CH_2CH_2S^-$ (2) $CH_3CH_2C(=O)-O^-$ (3)

(a) 3 >1 > 2
(b) 2 > 3 > 1
(c) 1 > 3 > 2
(d) 2 > 1 > 3

28. Identify products of the given reactions :

Reaction-1 $\xrightarrow[CH_3CO_2H]{CH_3CO_2Na}$ Product

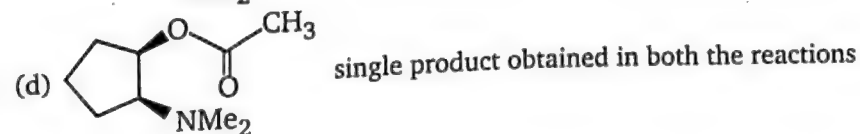
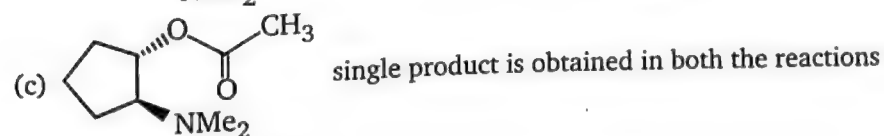
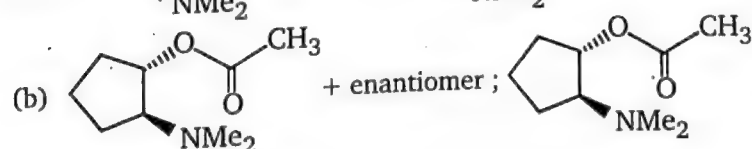
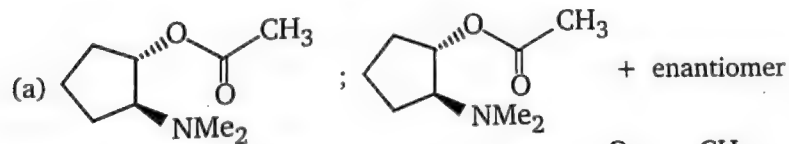
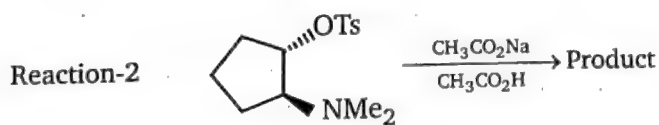
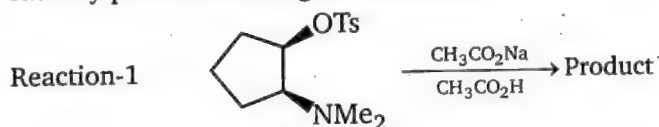
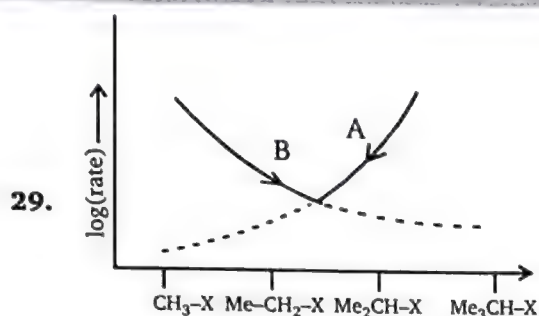
Reaction-2 $\xrightarrow[CH_3CO_2H]{CH_3CO_2Na}$ Product

(a) ; + enantiomer

(b) + enantiomer ;

(c) single product is obtained in both the reactions

(d) single product obtained in both the reactions

29.

Which of the following is true about given graphs A and B ?

(a) $A \rightarrow S_{N^1}$ $B \rightarrow S_{N^2}$
(b) $A \rightarrow S_{N^2}$, $B \rightarrow S_{N^1}$
(c) A & $B \rightarrow E_1$
(d) A & $B \rightarrow E_2$

30. In each of the following groups, which is the strongest (best) nucleophile ?

(I) (1) H_3C-O^- (2) $CH_3CH_2O^-$ (3) H_3C-S^- in CH_3OH

(II) (1) OH^- (2) H_2O (3) NH_2^- in DMF

(III) (1) $(CH_3)_2CH-CH(CH_3)-O^-$ (2) $(CH_3)_3C-O^-$ (3) CH_3O^- in DMSO

(a) I,3 ; II,3 ; III,2
(b) I,2 ; II,1 ; III,3
(c) I,1; II,2 ; III,1
(d) I,3 ; II,1 ; III,3

31. $C_6H_5-SO_2-(CH_2)_4-CH_2-Cl \xrightarrow[\text{dimethoxy ethane}]{NaNH_2}$ (A) (Major) ; Product (A) is :

(a) $C_6H_5-SO_2-(CH_2)_3-CH=CH_2$
(b) $C_6H_5-SO_2-$cyclopentyl
(c) $C_6H_5-SO_2-(CH_2)_4-CH_2-NH_2$
(d) None of these

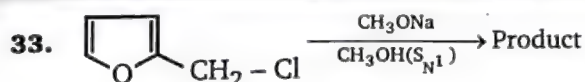
32. Which of the following reaction is an elimination reaction ?

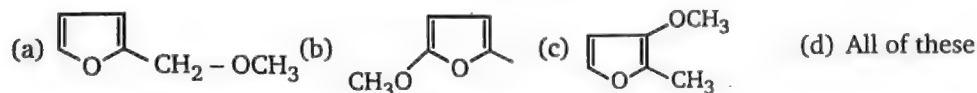
(a) Cyclohexanol $\xrightarrow{H_2SO_4}$ Cyclohexene + H

(b)

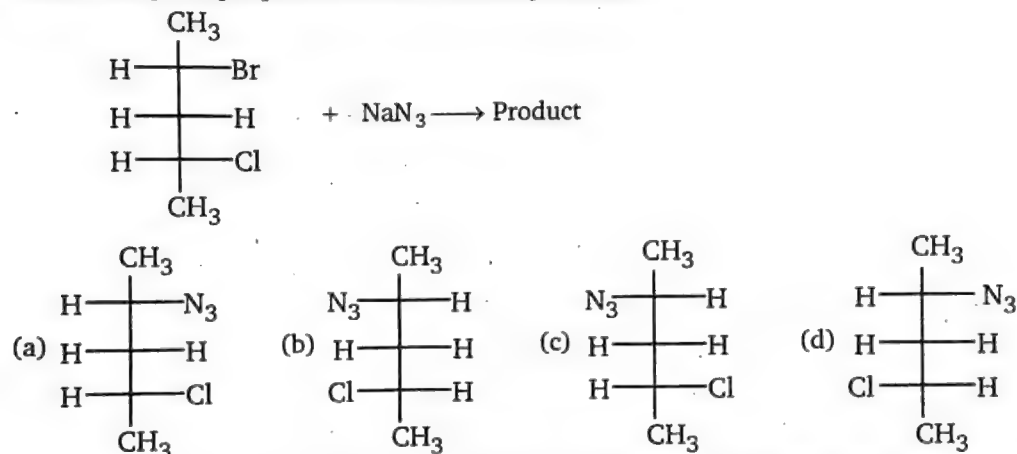
(c) Bromocyclohexane $\xrightarrow{NaOCH_3}$ Methoxycyclohexane (OCH_3)

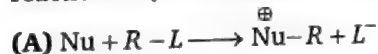
(d) both (a) and (b)

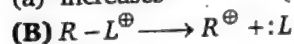
33. (2-furyl)$-CH_2-Cl \xrightarrow[CH_3OH(S_{N}1)]{CH_3ONa}$ Product

Which of the following products can be obtained from above reaction ?

(a) (2-furyl)$-CH_2-OCH_3$ (b) CH_3O-(furan)- (c) (furan with OCH_3 and CH_3) (d) All of these

34. What is the principal product of the following reaction ?

$+ \; NaN_3 \longrightarrow$ Product

(a) (b) (c) (d)

35. What would be the effect of increasing solvent polarity on the rate of each of the following reactions ? (Nu = neutral nucleophile)

(A) $Nu + R-L \longrightarrow \overset{\oplus}{Nu}-R + L^-$

(a) increases (b) decreases (c) constant (d) can not be predicted

(B) $R-L^{\oplus} \longrightarrow R^{\oplus} + :L$

(a) increases (b) decreases (c) constant (d) cannot predict

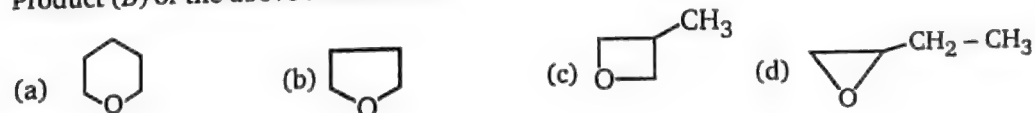
36. Which of the following is most reactive toward $S_{N}2$ reaction ?

(a) $CH_2=CH-CH_2-Cl$ (b) $Ph-CH_2-Cl$

(c) $Me-O$⌒Cl (d) $Ph-\underset{\underset{O}{\|}}{C}-CH_2-Cl$

37. 4-chloro-1-butanol + NaOH $\longrightarrow$ (*B*)

Product (*B*) of the above reaction is :

(a) (b) (c) (d)

38. In the given pairs of alkyl-halide, in which pair the first compound is more reactive than second compound toward S_{N^2} reaction ?

(a) $(CH_3)_2CHBr$ or $CH_3-CH_2-CH_2-Br$
(b) $CH_3-CH_2-CH_2-Br$ or $CH_3-CH_2-CH_2-I$
(c) $Ph-Br$ or $CH_3-CH_2-CH_2-Br$
(d) $CH_2=CH-CH_2-Cl$ or $H_2C=CH-\dot{C}l$

39. In the given pair of reaction in which pair the second reaction is more reactive than first toward S_{N^2} reaction ?

(a) $CH_3-CH_2-Cl+CH_3-CH_2-O^- \longrightarrow Et-O-Et$ (or)
$CH_2-CH_2-Cl+CH_3-CH_2-OH \longrightarrow Et-O-Et$
(b) $CH_3-CH_2-Cl+EtO^- \longrightarrow Et-O-Et$ (or)
$CH_3-CH_2-Cl+EtS^- \longrightarrow CH_3-CH_2-S-Et$
(c) $\underset{(1m)}{Et-Cl}+\underset{(2m)}{CH_3O^-} \longrightarrow Et-O-CH_3$ (or)
$\underset{(2m)}{Et-Cl}+\underset{(1m)}{CH_3O^-} \longrightarrow Et-O-CH_3$
(d) $Et-Br+Ph_3P \longrightarrow Et-\overset{\oplus}{P}Ph_3$ (or)
$Et-Br+Ph_3N \longrightarrow E+-\overset{\oplus}{N}Ph_3$

40. Among the following pair of reactions in which pair the second reaction is more reactive than first in S_{N^1} reaction ?

(a) $Me_3CCl+H_2O \longrightarrow Me_3COH$ (or) $Me_3CBr+H_2O \longrightarrow Me_3COH$
(b) $Me_3CCl+CH_3OH \longrightarrow Me_3C-OCH_3$ (or) $Me_3C-Cl+H_2O \longrightarrow Me_3C-OH$
(c) $\underset{(1M)}{Me_3CCl}+H_2O \longrightarrow$ (or) $\underset{(2M)}{Me_3CCl}+H_2O$
(d) All of these

41. Which is a true statement concerning the transition state of an S_{N^2} reaction ?

(a) Closely resembles a carbocation intermediate
(b) The electrophile is responsible for the reaction
(c) Lower is energy than the starting materials
(d) Involves both the nucleophile and electrophile

42. Increasing the concentration of a nucleophile in a typical S_{N^2} reaction by a factor of 10 will cause the reaction rate to :

(a) increase by a factor of 10
(b) increase by a factor of 10^2
(c) decrease by a factor of 10
(d) remain about the same

43. Decreasing the concentration of an electrophile in a typical S_{N^2} reaction by a factor of 3 will cause the reaction ratio to :

(a) increase by a factor of 3
(b) increase by a factor of 3^2
(c) decrease by a factor of 3
(d) remain about the same

44. Increasing the concentration of an electrophile in a typical S_{N^2} reaction by a factor of 3 and the concentration of the nucleophile by a factor of 3 will change the reaction rate to :

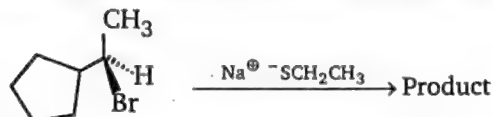
(a) increase by a factor of 6 (b) increase by a factor of 9

(c) decrease by a factor of 3 (d) remain about the same

45. Consider the following reaction and select the best choice that represents the reaction.

(Cyclopentyl–C(CH_3)(H)(Br)) $\xrightarrow{Na^{\oplus}\ {}^{-}SCH_2CH_3}$ Product

(a) Cyclopentyl–C(CH_3)(H)(SCH_2CH_3) (b) 2-Methylcyclopentyl–C(CH_3)(H)(SCH_2CH_3)

(c) Cyclopentyl–C(CH_3)(SCH_2CH_3)(H) (d) 2-Methylcyclopentyl–C(CH_3)($S-CH_2CH_3$)(H)

46. Fischer projection (top: I; Me–H; Et–D; bottom: H) $\xrightarrow{KSH}$ Product; Identify the product.

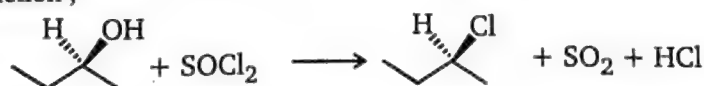
(a)

(b) H; Me–H; Et–D; SH

(c)

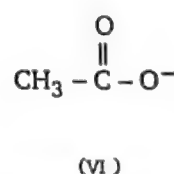
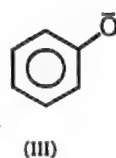
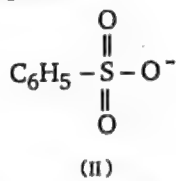
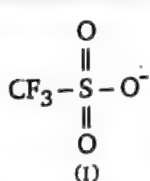
(d) SH; H–Me; Et–D; H

47. The reaction ,

(H, OH alcohol) + $SOCl_2$ $\longrightarrow$ (H, Cl chloride) + SO_2 + HCl

proceeds by the........... mechanism.

(a) S_{N^i} (b) S_{N^2} (c) S_{E^2} (d) S_{N^1}

48. Consider the following anions.

$CF_3-SO_2-O^-$ (I) $C_6H_5-SO_2-O^-$ (II) $C_6H_5O^-$ (III) CH_3-CO-O^- (VI)

When attached to sp^3-hybridized carbon, their leaving group ability in nucleophilic substitution reaction decreases in the order :

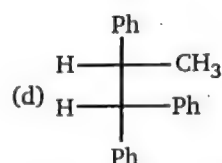
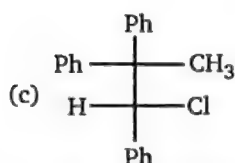
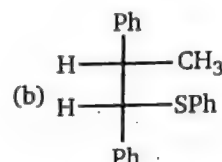
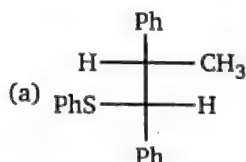
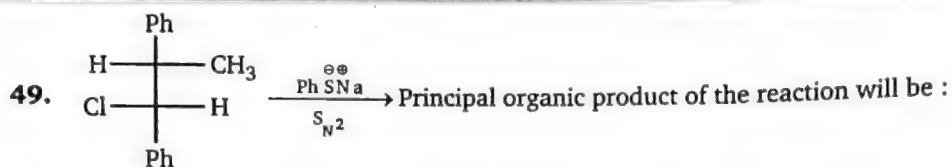
(a) I > II > III > IV (b) I > II > IV > III (c) IV > I > II > III (d) IV > III > II > I

49. Fischer projection: Ph (top); H—C—CH_3; Cl—C—H; Ph (bottom) $\xrightarrow[S_N2]{Ph\overset{\ominus}{S}\overset{\oplus}{Na}}$ Principal organic product of the reaction will be :

(a)

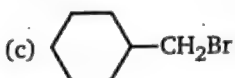
(b)

(c)

(d)

50. Reaction of *R*-2-butanol with *p*-toluenesulphonyl chloride in pyridine followed by reaction with LiBr gives:

(a) *R*-2-butyl bromide
(b) *S*-2-butyl tosylate
(c) *R*-2-butyl tosylate
(d) *S*-2-butyl bromide

51. The compound which undergoes S_{N^1} reaction most rapidly is :

(a) cyclohexyl—Br
(b) cyclohexenyl—Br
(c) cyclohexyl—CH_2Br
(d) bicyclic (bridgehead)—Br

52. Addition of KI accelerates the hydrolysis of primary alkyl halides because :

(a) KI is soluble in organic solvents
(b) the iodide ion is a weak base and a poor leaving group
(c) the iodide ion is a strong base
(d) the iodide ion is a powerful nucleophile as well as a good leaving group

53. Which of the following phrases are not correctly associated with S_{N^1} reaction ?

(1) Rearrangement is possible
(2) Rate is affected by polarity of solvent
(3) The strength of the nucleophile is important in determining rate
(4) The reactivity series is tertiary > secondary > primary
(5) Proceeds with complete inversion of configuration

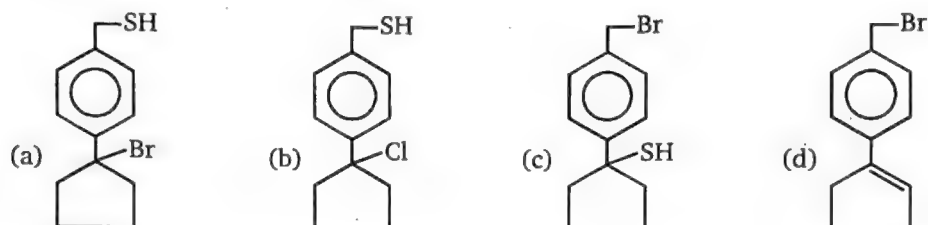
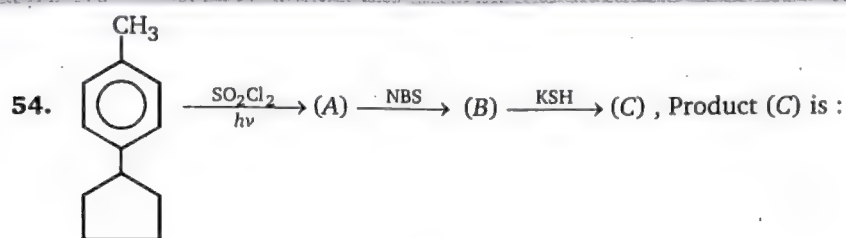
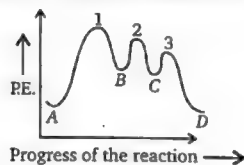
(a) 3, 5
(b) 5 only
(c) 2, 3, 5
(d) 3 only

54. CH_3 (on benzene ring bearing cyclopentyl) $\xrightarrow[h\nu]{SO_2Cl_2}$ (*A*) $\xrightarrow{NBS}$ (*B*) $\xrightarrow{KSH}$ (*C*) , Product (*C*) is :

(a)

(b)

(c)

(d)

55. Energy profile diagram for an exothermic reaction, $A \xrightarrow{1} B \xrightarrow{2} C \xrightarrow{3} D$, is given below.

The rate determining step of the reaction is :

(a) $A \longrightarrow B$ (b) $B \longrightarrow C$ (c) $C \longrightarrow D$ (d) can not predict

56. CH_3 (tetralin) $\xrightarrow{NBS}$ (*A*) Major

Major product is (*A*) is :

(a)

(b)

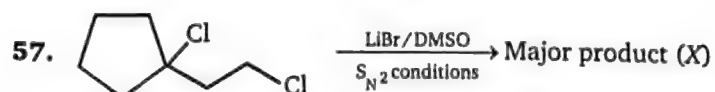
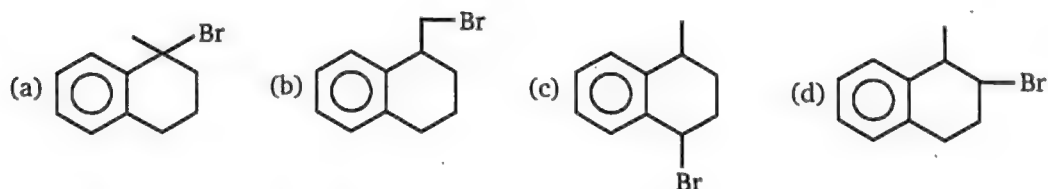
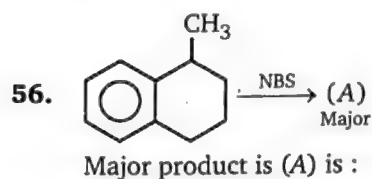
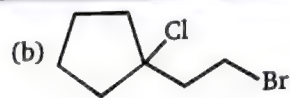
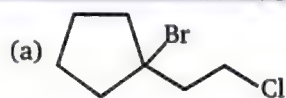
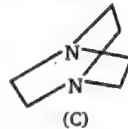
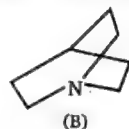
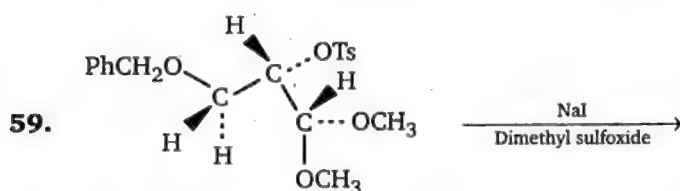
(c)

(d)

57. Cl, Cl $\xrightarrow[S_N2 \text{ conditions}]{LiBr/DMSO}$ Major product (*X*)

The product *X* is :

(a) Br, Cl (b) Cl, Br

(c) Br, Br (d) Cl

58. Relative rate of reaction of the following amine with methyl iodide is:

(a) A > B > C (b) A > C > B (c) B > C > A (d) B > A > C

59.

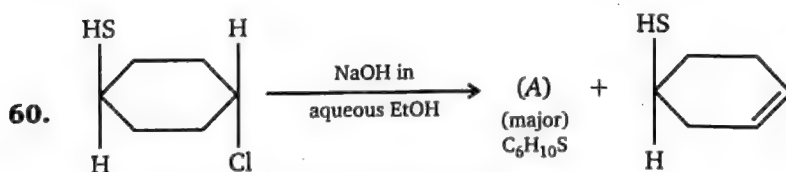
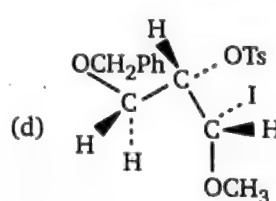
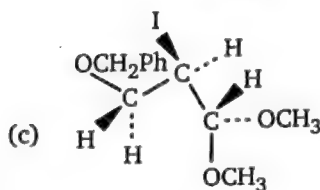
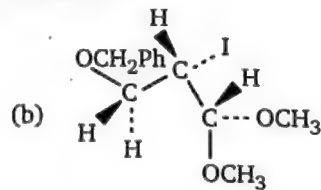
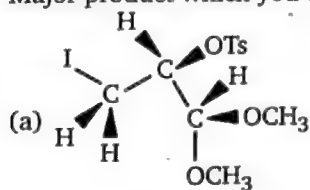
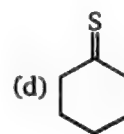
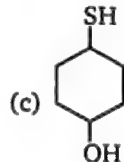
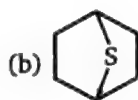
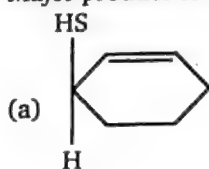
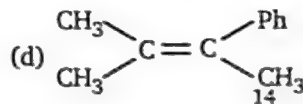
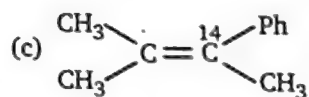
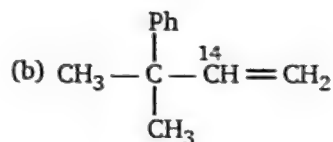
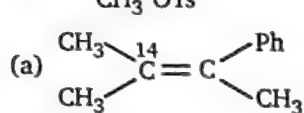
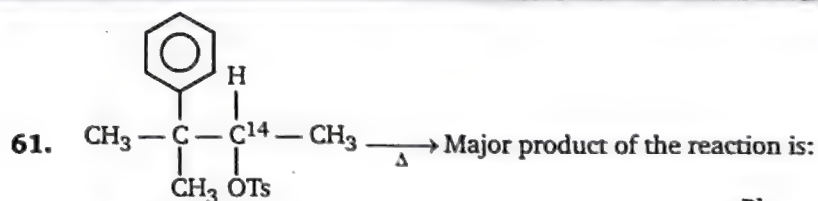
60. HS, H, H, Cl $\xrightarrow[\text{aqueous EtOH}]{\text{NaOH in}}$ (A) (major) $C_6H_{10}S$ + HS, H

Major product of the above reaction is :

(a) HS, H (b) S (c) SH, OH (d) S

61. $CH_3-\underset{CH_3}{\overset{Ph}{C}}-\underset{OTs}{\overset{H}{C^{14}}}-CH_3 \xrightarrow{\Delta}$ Major product of the reaction is:

(a) $(CH_3)_2\overset{14}{C}=C(Ph)(CH_3)$ (b) $CH_3-\underset{CH_3}{\overset{Ph}{C}}-\overset{14}{C}H=CH_2$

(c) $(CH_3)_2C=\overset{14}{C}(Ph)(CH_3)$ (d) $(CH_3)_2C=C(Ph)(\overset{14}{C}H_3)$

62. The decreasing order of reactivity of the compounds given below towards solvolysis under identical conditions is :

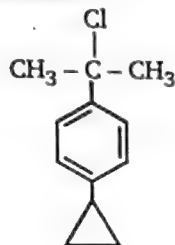
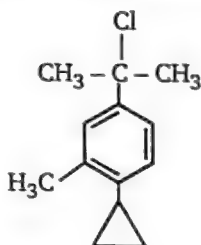
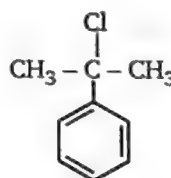
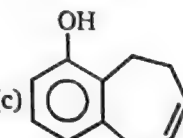
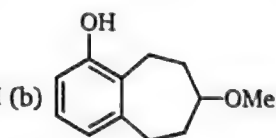
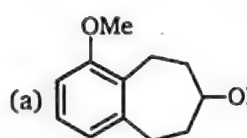
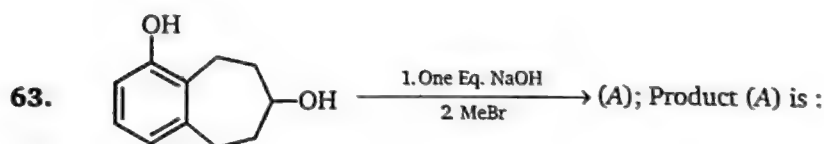
(I) $CH_3-\overset{Cl}{C}-CH_3$ attached to a benzene ring bearing a para-cyclopropyl group

(II) $CH_3-\overset{Cl}{C}-CH_3$ attached to a benzene ring bearing a para-cyclopropyl group and an H_3C group ortho to the cyclopropyl

(III) $CH_3-\overset{Cl}{C}-CH_3$ attached to a benzene ring

(a) II > III > I (b) I > II > III (c) III > II > I (d) II > I > III

63. (OH-substituted benzo-fused seven-membered ring bearing –OH) $\xrightarrow[\text{2 MeBr}]{\text{1. One Eq. NaOH}}$ (*A*); Product (*A*) is :

(a) (b) (c)

(d) None of these

64. (*R*)-2-octyl tosylate is solvolyzed in water under ideal S_{N^1} conditions. The product(s) will be:

(a) *R*-2-octanol and *S*-2-octanol in a 1 : 1 ratio
(b) *R*-2-octanol and *S*-2-octanol in a 1.5 : 1 ratio
(c) *R*-2-octanol only
(d) *S*-2-octanol only

65. From each of the following pairs select the compound that will react faster with sodium iodide in acetone :

Pair-A: (1) 2-Chloropropane (2) 2-Bromopropane

Pair-B: (3) 1-Bromobutane (4) 2-Bromobutane

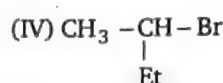
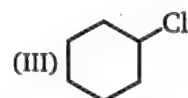
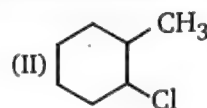
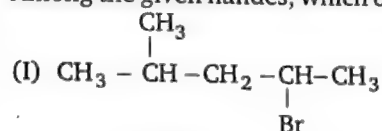
(a) 1, 3 (b) 1, 4 (c) 2, 3 (d) 2, 4

66. Among the given halides, which one will give same product in both S_N1 and S_N2 reactions.

(I) $CH_3-CH(CH_3)-CH_2-CH(Br)-CH_3$

(II) 1-methyl-2-chlorocyclohexane (CH_3, Cl on ring)

(III) Chlorocyclohexane

(IV) $CH_3-CH(Et)-Br$

(a) (III) only (b) (I) & (II) (c) (III) & (IV) (d) (I), (III) & (IV)

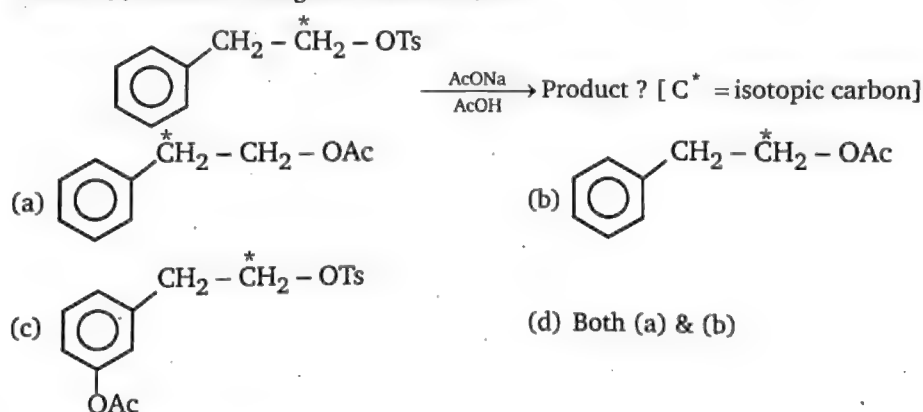
67. Product(s) formed during this reaction is/are :

$C_6H_5-CH_2-\overset{*}{C}H_2-OTs \xrightarrow[AcOH]{AcONa}$ Product ? [C^* = isotopic carbon]

(a) $C_6H_5-\overset{*}{C}H_2-CH_2-OAc$

(b) $C_6H_5-CH_2-\overset{*}{C}H_2-OAc$

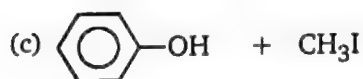
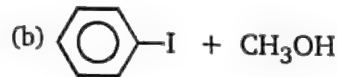
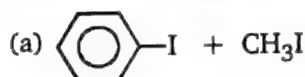
(c) $AcO-C_6H_4-CH_2-\overset{*}{C}H_2-OTs$ (OAc on ring)

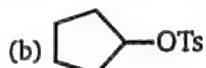
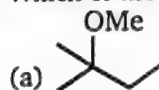
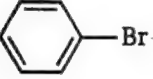
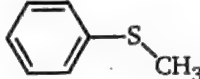
(d) Both (a) & (b)

68. Anisole $\xrightarrow[\text{reflux}]{\text{excess HI (conc.)}}$ Product

(a) $C_6H_5-I + CH_3I$

(b) $C_6H_5-I + CH_3OH$

(c) $C_6H_5-OH + CH_3I$

(d) $C_6H_5-OH + CH_3CH_2I$

69. Which of the following compounds would react faster with NaCN in an S_N2 reaction ?

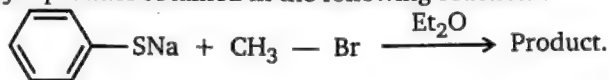
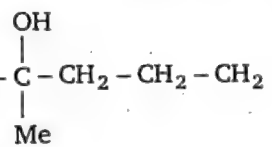
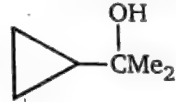
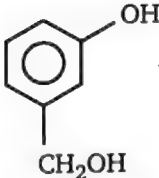
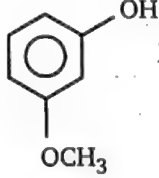
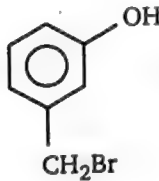
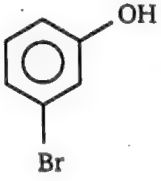
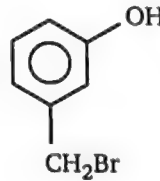
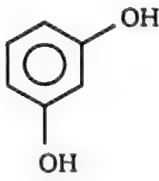
(a) $(CH_3)_2C(OMe)CH_2CH_3$ (b) Cyclopentyl–OTs (c) MeO–$CH_2CH_2CH_2CH_3$ (d) $CH_3CH_2CH_2$–OTs

70. $HC \equiv CNa + Cl-CH_2-CH_2-CH_2-I \longrightarrow (A)$; Major product (A) is :

(a) $H-C \equiv C-CH_2-CH_2-CH_2-I$
(b) $CH_2=CH-CH_2-I$
(c) $H-C \equiv C-CH_2-CH_2-CH_2-Cl$
(d) $CH_2=CH-CH_2-Cl$

71. What is the major product obtained in the following reaction ?

$$C_6H_5-SNa + CH_3-Br \xrightarrow{Et_2O} \text{Product.}$$

(a) benzyne (b) C_6H_5-Br (c) $C_6H_5-S-CH_3$ (d) C_6H_6

72. (Br, H)-cyclohexane-(CH$_3$, H) $+ OH^- \xrightarrow{S_N2} A$; The product A is :

(a) HO, H / CH$_3$, H (cyclohexane)
(b) H, HO / CH$_3$, H (cyclohexane)
(c) Both (a) and (b) are correct
(d) None is correct

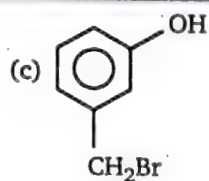
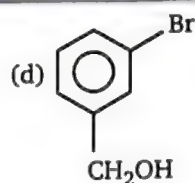
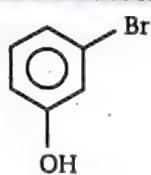
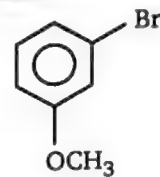
73. $Me_2C=CH-CH_2-CH_2-Cl \xrightarrow[CaCO_3]{H_2O} (X)$; Major product of the reaction is :

(a) $Me-C(OH)(Me)-CH_2-CH_2-CH_2$
(b) $Me_2C=CH-CH_2-CH_2-OH$
(c) $Me_2C=CH-CH(OH)-CH_2-OH$
(d) cyclopropyl$-CMe_2(OH)$

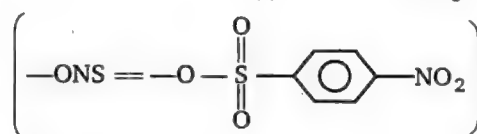
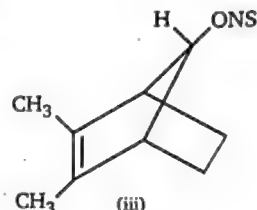
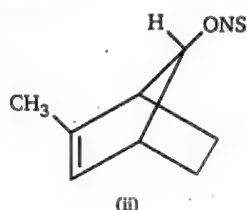
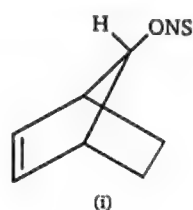
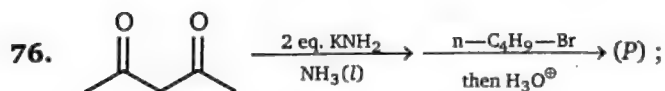
74. 3-(CH$_2$OH)phenol $\xrightarrow[\Delta]{HBr} (A)$, 3-(OCH$_3$)phenol $\xrightarrow[\Delta]{HBr} (B)$

Product (A) and (B) respectively are :

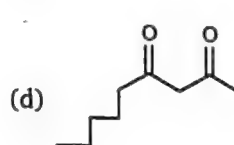
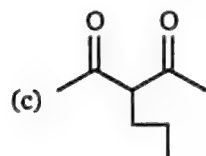
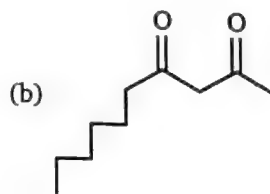
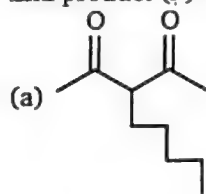
(a) 3-(CH$_2$Br)phenol and 3-Br-phenol
(b) 3-(CH$_2$Br)phenol and 3-OH-phenol

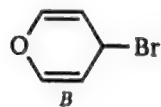
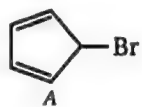
(c) [3-(bromomethyl)phenol] and [3-bromophenol] (d) [3-bromobenzyl alcohol] and [3-bromoanisole]

75. Relative rate of reaction with H_2O.

(a) (i) > (ii) > (iii)
(b) (ii) > (i) > (iii)
(c) (iii) > (ii)> (i)
(d) (iii) > (i) > (ii)

76. [pentane-2,4-dione] $\xrightarrow[NH_3(l)]{2\text{ eq. } KNH_2}$ $\xrightarrow[\text{then } H_3O^{\oplus}]{n-C_4H_9-Br}$ (P) ;

End product (P) of the above reaction is :

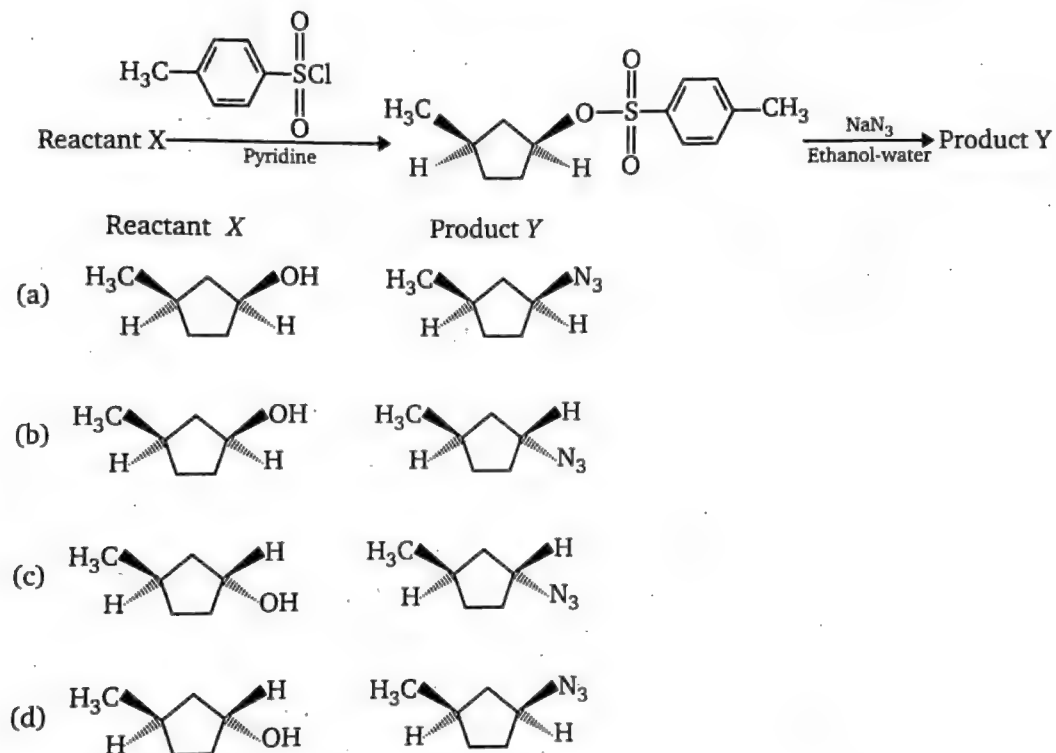
(a) (b)

(c) (d)

77. Which of the following statements is correct regarding the rate of hydrolysis of the compounds (A) and (B) by S_{N^1} reaction ?

A: [5-bromocyclopenta-1,3-diene]—Br B: [4-bromo-4H-pyran] O—Br

(a) A reacts faster than B (b) B reacts faster than A
(c) Both A and B reacts at the same rate (d) Neither A nor B reacts

78. What are reactant X and product Y in the following sequence of reactions ?

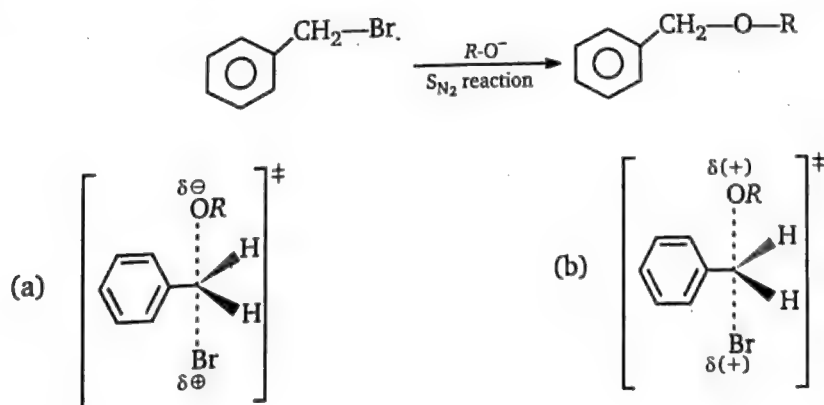
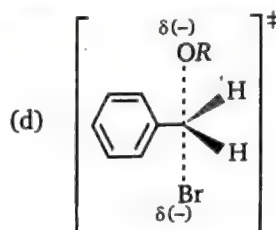
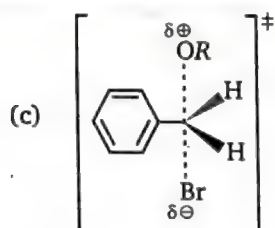
Reactant X —(H_3C–C_6H_4–SO_2Cl, Pyridine)→ [cyclopentyl tosylate with H_3C, H, H] —(NaN_3, Ethanol-water)→ Product Y

	Reactant X	Product Y
(a)	H_3C, H, OH, H	H_3C, H, N_3, H
(b)	H_3C, H, OH, H	H_3C, H, H, N_3
(c)	H_3C, H, H, OH	H_3C, H, H, N_3
(d)	H_3C, H, H, OH	H_3C, H, N_3, H

79. Transition state of given S_{N_2} is :

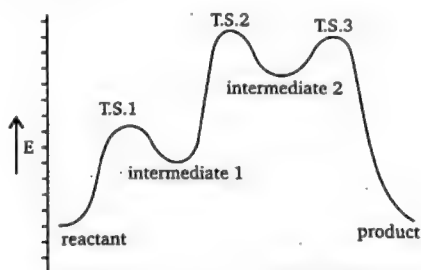
C_6H_5–CH_2–Br $\xrightarrow[S_{N_2}\text{ reaction}]{R\text{-}O^-}$ C_6H_5–CH_2–O–R

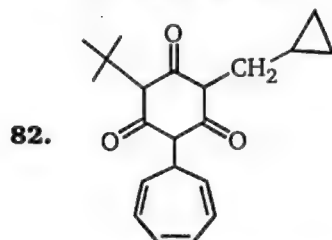
(a) $[\delta\ominus\ OR \cdots C(H)(H)(C_6H_5) \cdots Br\ \delta\oplus]^{\ddagger}$

(b) $[\delta(+)\ OR \cdots C(H)(H)(C_6H_5) \cdots Br\ \delta(+)]^{\ddagger}$

(c) $\left[\begin{array}{c} \delta\oplus \\ OR \\ \vdots \\ C_6H_5-C(H)(H) \\ \vdots \\ Br \\ \delta\ominus \end{array} \right]^{\ddagger}$ (d) $\left[\begin{array}{c} \delta(-) \\ OR \\ \vdots \\ C_6H_5-C(H)(H) \\ \vdots \\ Br \\ \delta(-) \end{array} \right]^{\ddagger}$

80. $C_6H_{13}Br + OH^- \longrightarrow C_6H_{13}OH + Br^-$ is an example of:

(a) Nucleophilic addition (b) Nucleophilic substitution
(c) Electrophilic addition (d) Electrophilic substitution
(e) Free radical substitution

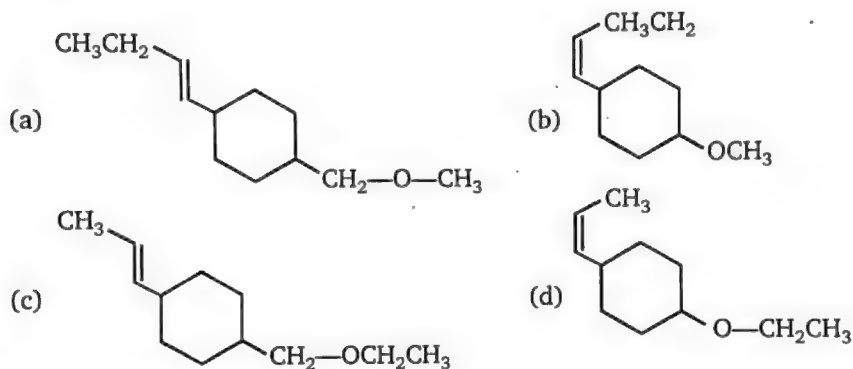
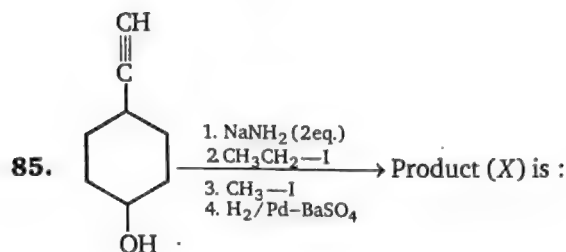
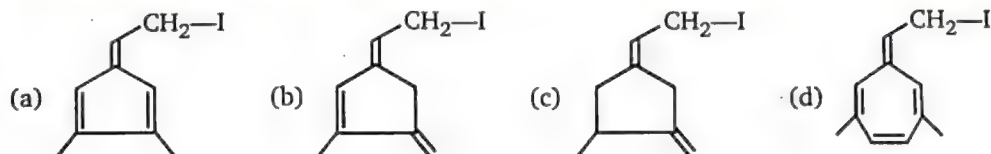
81. Transition state 2 is structurally most likely as :

(a) intermediate 1 (b) transition state 3
(c) intermediate 2 (d) product

82.

x = Number of aromatic compound obtained when above compound undergo complete acidic hydrolysis.

(a) 1 (b) 2 (c) 3 (d) 4

83. S_N1 and S_N2 reactions are

(a) Both stereospecific
(b) Both stereoselective
(c) Stereoselective and stereospecific respectively
(d) Stereospecific and stereoselective respectively

84. Most reactive compound toward S_{N^1} is :

ANSWERS — LEVEL 1															
1.	(a)	**2.**	(b)	**3.**	(c)	**4.**	(a)	**5.**	(b)	**6.**	(b)	**7.**	(b)	**8.**	(d)
9.	(b)	**10.**	(a)	**11.**	(c)	**12.**	(a)	**13.**	(d)	**14.**	(d)	**15.**	(b)	**16.**	(c)
17.	(a)	**18.**	(a)	**19.**	(c)	**20.**	(d)	**21.**	(b)	**22.**	(a)	**23.**	(c)	**24.**	(c)
25.	(d)	**26.**	(d)	**27.**	(d)	**28.**	(a)	**29.**	(a)	**30.**	(d)	**31.**	(b)	**32.**	(d)
33.	(d)	**34.**	(c)	**35.**	A(a)	**35.**	B(b)	**36.**	(d)	**37.**	(b)	**38.**	(d)	**39.**	(b)
40.	(d)	**41.**	(d)	**42.**	(a)	**43.**	(c)	**44.**	(b)	**45.**	(c)	**46.**	(d)	**47.**	(a)
48.	(b)	**49.**	(b)	**50.**	(d)	**51.**	(b)	**52.**	(d)	**53.**	(a)	**54.**	(b)	**55.**	(a)
56.	(a)	**57.**	(b)	**58.**	(c)	**59.**	(c)	**60.**	(b)	**61.**	(c)	**62.**	(d)	**63.**	(a)
64.	(b)	**65.**	(c)	**66.**	(d)	**67.**	(d)	**68.**	(c)	**69.**	(d)	**70.**	(c)	**71.**	(c)
72.	(b)	**73.**	(d)	**74.**	(b)	**75.**	(c)	**76.**	(d)	**77.**	(b)	**78.**	(b)	**79.**	(d)
80.	(b)	**81.**	(c)	**82.**	(b)	**83.**	(b,c)	**84.**	(d)	**85.**	(b)				

1. **Statement-1 :** Nucleophilicity order in polar-protic solvent is $I^- < Br^- < Cl^- < F^-$

Statement-2 : Due to bigger size of I^- it is less solvated in polar-protic solvent.

(a) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(b) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(c) Statement-1 is true, statement-2 is false.

(d) Statement-1 is false, statement-2 is true.

2. **Statement - 1 :** $CH_3-CH_2-Cl + NaI \xrightarrow{\text{Acetone}} CH_3-CH_2-I + NaCl\downarrow$

Statement- 2 : Acetone is polar-protic solvent and solubility order of sodium halides decreases dramatically in order NaI > NaBr > NaCl. The last being virtually insoluble in this solvent and a 1° and 2° chloro alkane in acetone is completely driven to the side of Iodoalkane by the precipitation reaction.

(a) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for statement-1.

(b) Statement-1 is true, Statement-2 is true and Statement-2 is Not the correct explanation for statement-1.

(c) Statement-1 is true, Statement-2 is false.

(d) Statement-1 is false, Statement-2 is true.

3. Encircle whichever of the following :

(a) is the stronger nucleophile (aprotic solvent) : F^- or I^-

(b) is the stronger nucleophile (protic solvent) : F^- or I^-

(c) is the stronger base : F^- or I^-

(d) is the stronger nucleophile (protic solvent) : NH_3 or NH_2NH_2

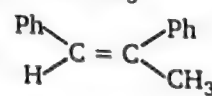
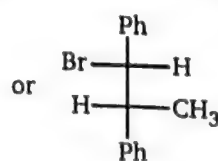
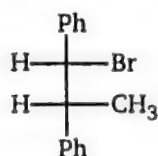
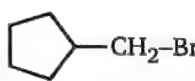
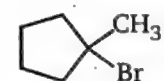
(e) is the better leaving group : CH_3COO^- or $CH_3SO_3^-$

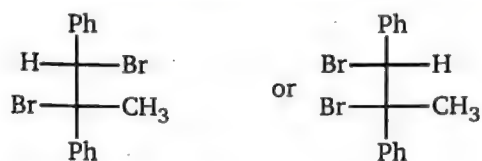
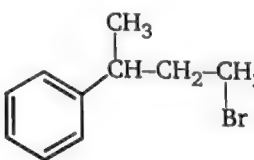
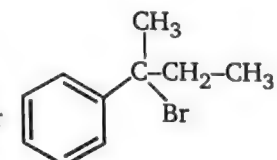
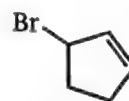
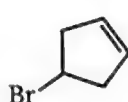
4. Encircle whichever of the following :

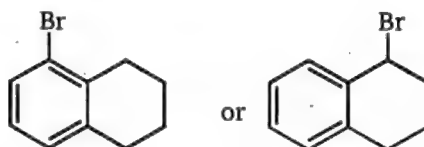
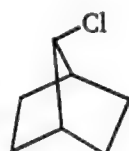
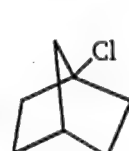
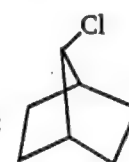
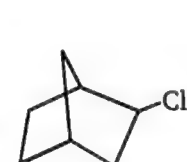
(a) undergoes an $S_{N}2$ reaction more rapidly, CH_3-Br or $CH_3-\underset{}{CH}(Br)-CH_3$

(b) undergoes an $S_{N}1$ reaction more rapidly, CH_3-Br or $CH_3-CH(Br)-CH_3$

(c) undergoes an E_2 reaction to give (Z)-1,2-diphenylpropene : Ph(H)C=C(Ph)CH_3

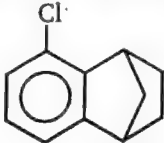
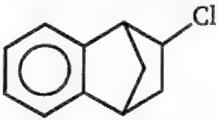
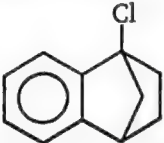
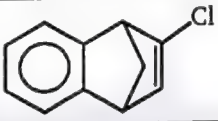
$$\begin{array}{c} Ph \\ H-\!\!\!\!-\!\!+\!\!-\!\!\!\!-Br \\ H-\!\!\!\!-\!\!+\!\!-\!\!\!\!-CH_3 \\ Ph \end{array} \quad \text{or} \quad \begin{array}{c} Ph \\ Br-\!\!\!\!-\!\!+\!\!-\!\!\!\!-H \\ H-\!\!\!\!-\!\!+\!\!-\!\!\!\!-CH_3 \\ Ph \end{array}$$

(d) reacts with NaI to give (Z)-1,2-diphenylpropene :

Ph; H—Br; Br—CH_3; Ph or Ph; Br—H; Br—CH_3; Ph

(e) undergoes an S_N1 reaction more rapidly,

Br or Br

5. Encircle whichever of the following :

(a) undergoes an S_N2 reaction more rapidly : $-CH_2-Br$ or CH_3, Br

(b) undergoes an E_1 reaction more rapidly : CH_3, $CH-CH_2-CH_2$, Br or CH_3, $C-CH_2-CH_3$, Br

(c) undergoes an S_N1 reaction more rapidly: Br or Br

(d) undergoes an S_N2 reaction more rapidly: Cl or Cl

(e) undergoes an E_2 reaction more rapidly : Cl or Cl

6. Match the column :

	Alkyl halide		Relative rate (S_{N^1})		Relative rate (S_{N^2})
(a)	CH_3-Br	**(p)**	1	**(w)**	1200
(b)	CH_3-CH_2-Br	**(q)**	1.05	**(x)**	40
(c)	$CH_3-CH(CH_3)-Br$	**(r)**	11	**(y)**	16
(d)	$CH_3-C(CH_3)_2-Br$	**(s)**	1,200000	**(z)**	1

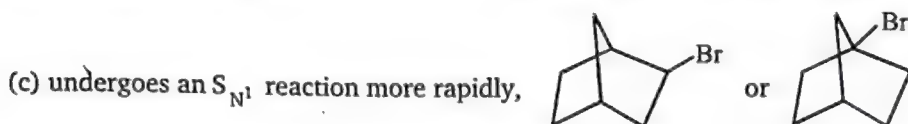
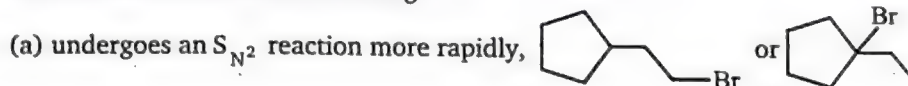
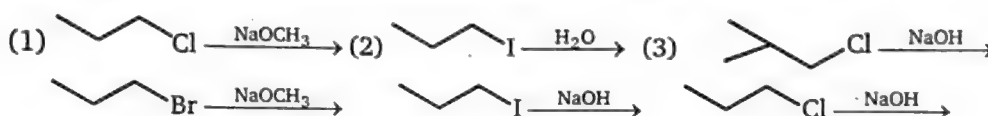
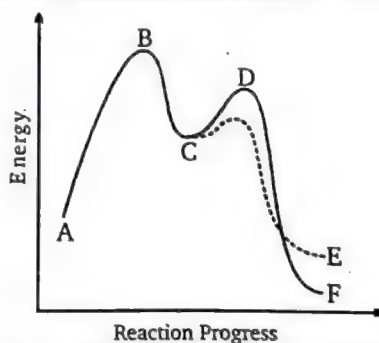
7. Matrix :

Column (I)		Column (II)	
	Compound		**Type of reaction**
(a)	Cl	**(p)**	S_{N^1} reaction can take place
(b)	Cl	**(q)**	S_{N^2} reaction can take place
(c)	Cl	**(r)**	S_{N^1} is not possible
(d)	Cl	**(s)**	S_{N^2} is not possible

8. Encircle whichever of the following :

(a) undergoes an S_N2 reaction more rapidly, (cyclopentyl–CH$_2$CH$_2$–Br) or (1-bromo-1-ethylcyclopentane)

(b) undergoes an S_N1 reaction more rapidly, $(CH_3)_3C-Br$ or $(CH_3)_3C-I$

(c) undergoes an S_N1 reaction more rapidly, (2-bromonorbornane) or (bromonorbornane, Br at bridgehead)

9. Reactivity : Circle the reaction that reacts FASTER by S_N2 in each pair :

10. Consider the potential energy diagram given below

(X) Name the positions A-D

(Y) Answer the following questions .

(i) Both reaction pathways are : EXOTHERMIC or ENDOTHERMIC

(ii) Which step is the rate determining step (RDS) ? B or D

(iii) Which product is most stable ? E or F

(iv) In accordance with Hammonds postulate, exothermic reactions tend to have

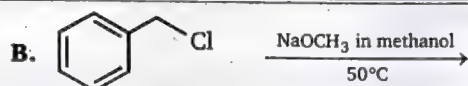
(a) early transition states that are reactant - like

(b) late transition states that are reactant-like

(c) early transition states that are product-like

(d) late transition states that are product-like.

11. Select whether the following combinations of reactants will react by substitution (S_{N^1} or S_{N^2} mechanism), elimination (E_1 or E_2 mechanism)

A. Cyclopentyl–Br $\xrightarrow[25°C]{\text{NaI in acetone}}$

(a) S_{N^1} (b) S_{N^2} (c) E_1 (d) E_2

B. $C_6H_5CH_2$–Cl $\xrightarrow[50°C]{NaOCH_3 \text{ in methanol}}$

(a) S_{N^1} (b) S_{N^2} (c) E_1 (d) E_2

C. Cyclohexyl–Cl $\xrightarrow[25°C]{NaOCH_3 \text{ in methanol}}$

(a) S_{N^1} (b) S_{N^2} (c) E_1 (d) E_2

D. $(CH_3)_3C-OH$ $\xrightarrow[25°C]{HBr\ 48\%\ \text{in}\ H_2O}$

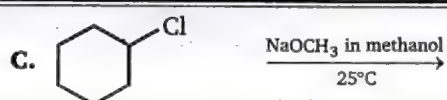
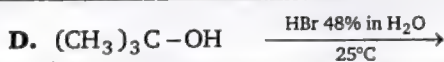
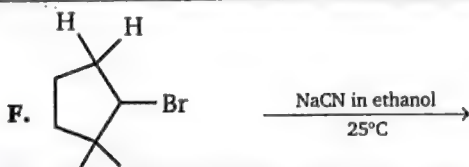
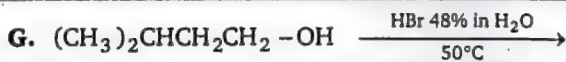
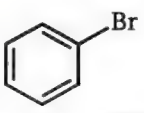
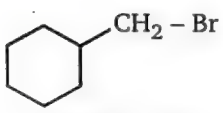
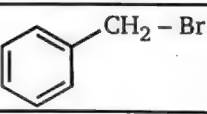
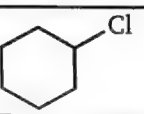
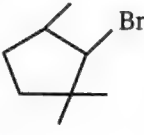
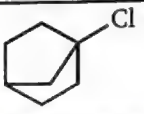
(a) S_{N^1} (b) S_{N^2} (c) E_1 (d) E_2

E. $(CH_3)_2CH-Br$ $\xrightarrow[25°C]{\text{NaCN in ethanol}}$

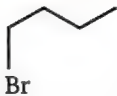
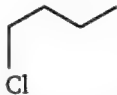
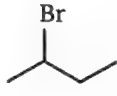
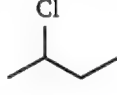
(a) S_{N^1} (b) S_{N^2} (c) E_1 (d) E_2

F. (H, H substituted cyclopentane with Br and dimethyl groups) –Br $\xrightarrow[25°C]{\text{NaCN in ethanol}}$

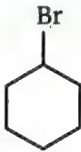
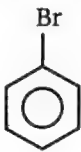
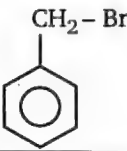
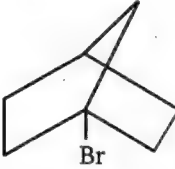
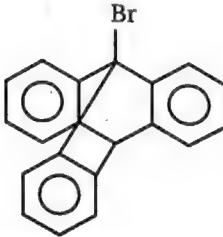
(a) S_{N^1} (b) S_{N^2} (c) E_1 (d) E_2

G. $(CH_3)_2CHCH_2CH_2-OH$ $\xrightarrow[50°C]{HBr\ 48\%\ \text{in}\ H_2O}$

(a) S_{N^1} (b) S_{N^2} (c) E_1 (d) E_2

12. Examine the ten structural formulas shown in fig. & select that satisfy each of the following conditions. Write one or more (a through j) in each answer box.

(a)	Br	**(b)**	CH_3 $H_3C-C-Cl$ CH_3	**(c)**	CH_2-Br
(d)	CH_3-I	**(e)**	CH_2-Br	**(f)**	Cl
(g)	CH_3 $H_3C-C-CH_2-Cl$ CH_3	**(h)**	$H_2C=C(CH_3)-CH_2-Cl$	**(i)**	Br
(j)	Cl				

A. Which compounds give an S_{N^2} substitution reaction on treatment with alcoholic NaSH ?

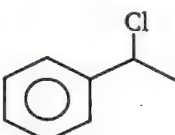
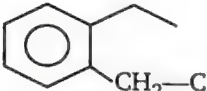
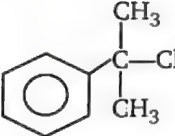
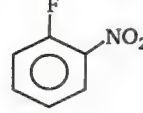
B. Which compounds give an E_2 elimination reaction on treatment with alcoholic KOH ?

C. Which compounds do not react under either of the previous reaction conditions ?

13. Select which reaction from the following reaction pairs will occur faster.

PART - 1	
Reaction A	I, CH_3 $\xrightarrow[\text{DMSO}]{H_2O}$ OH, CH_3
Reaction B	I, H $\xrightarrow[\text{DMSO}]{H_2O}$ OH, H

PART - 2	
Reaction C	Cl, CH_3 $\xrightarrow[\text{DMSO}]{\text{NaI}}$ I, CH_3
Reaction D	CH_2Cl $\xrightarrow[\text{DMSO}]{\text{NaI}}$ CH_2I

PART - 3	
Reaction E	I, H $\xrightarrow[\text{DMSO}]{\text{NaCl}}$ Cl, H
Reaction F	I, H $\xrightarrow[\text{EtOH}]{\text{NaCl}}$ Cl, H

PART - 4	
Reaction G	I, H $\xrightarrow[\text{DMSO}]{NaN_3}$ N_3, H
Reaction H	Br, H $\xrightarrow[\text{DMSO}]{NaN_3}$ N_3, H

PART - 5	
Reaction I	$C_6H_5CH_2-Cl \xrightarrow[\text{acetone}]{NaI} C_6H_5CH_2-I$
Reaction J	$p\text{-}CH_3C_6H_4Br \xrightarrow[\text{acetone}]{NaI} p\text{-}CH_3C_6H_4I$

14. Tick your answer in the given box.

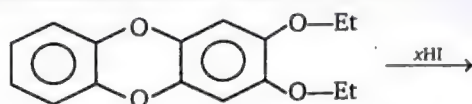
	Alkyl Halide	2-D Structure		Expect S_{N^2} (at a reasonable rate)
(a)	1-Bromobutane	Br		Yes
				No
(b)	1- Chlorobutane	Cl		Yes
				No
(c)	2-Bromobutane	Br		Yes
				No
(d)	2-Chlorobutane	Cl		Yes
				No
(e)	2-Chloro-2-methyl propane	Cl		Yes
				No

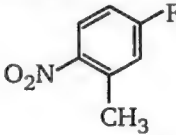
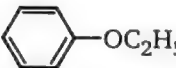
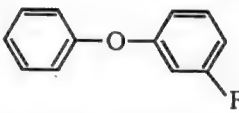
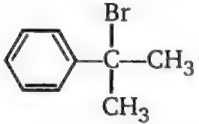
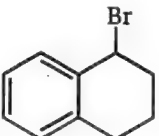
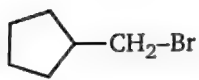
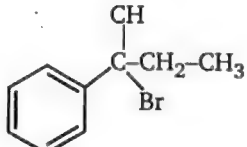
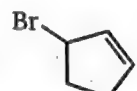
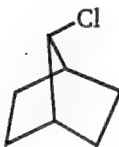
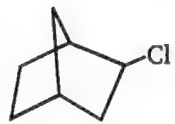
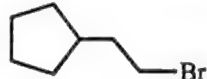
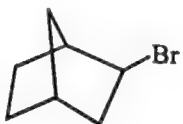
(f)	Bromocyclohexane	Br		Yes
				No
(g)	Bromobenzene	Br		Yes
				No
(h)	Benzyl bromide	CH_2-Br		Yes
				No
(i)	1-Bromo-2,2-dimethyl propane	Br		Yes
				No
(j)	Bicyclo compound	Br		Yes
				No
(k)	1-bromotriptycene	Br		Yes
				No

15. Match the column

	Column-I		Column-II
(a)	Cl	**(p)**	It will undergo Nucleophilic Substitution reaction
(b)	CH_2—Cl	**(q)**	It will undergo E_2 reaction
(c)	CH_3 — C — Cl, CH_3	**(r)**	It will undergo E_1 reaction
(d)	F, NO_2	**(s)**	It will undergo S_{N^2} reaction
		(t)	It will undergo S_{N^1} reaction

16.

O, O, O—Et, O—Et $\xrightarrow{xHI}$

How many (x) moles of HI consumed?

17.

	Column (I)		Column (II)
(a)	Ph–C(Et)(Et)–Cl $\xrightarrow{H_2O}$	**(p)**	S_{N^1}
(b)	1-chlorobutane $\xrightarrow{Ph-\overset{\ominus\oplus}{S}Na}$	**(q)**	S_{N^2}
(c)	o-fluoronitrosobenzene (F, NO) $\xrightarrow[\Delta]{KOH}$	**(r)**	Carbocation is intermediate
(d)	cis-2-butene $\xrightarrow[CCl_4]{Br_2}$	**(s)**	Carbanion is intermediate

18.

	Column (I) (Reaction sequence)		Column (II) (Reagent required)
(a)	$(CH_3)_3C-O^{\ominus} \longrightarrow (CH_3)_3C-OEt$	**(p)**	$EtO^{\ominus}$
(b)	$(CH_3)_3C-Br \longrightarrow (CH_3)_2C=CH_2$	**(q)**	EtBr
(c)	$(CH_3)_2C=CH_2 \longrightarrow (CH_3)_3C-OEt$	**(r)**	$EtOH/H^{\oplus}$
(d)	Et — Cl $\longrightarrow$ n-butane	**(s)**	Et–Cl/Na ether

19. Choose the one compound within each set that meets the indicated criterion :

	Column (I)		Column (II)
(a)	The compound that reacts with alcoholic KOH to liberate Halide ion through substitution reaction.	**(p)**	O_2N–benzene ring bearing F and CH_3
(b)	The compound that cannot be prepared by a Williamson ether synthesis.	**(q)**	C_6H_5–OC_2H_5
(c)	The compound that gives an acidic solution when allowed to stand in aqueous ethanol.	**(r)**	C_6H_5–O–C_6H_4–F
(d)	The ether that cleaves more rapidly in HI.	**(s)**	C_6H_5–C(Br)(CH_3)–CH_3

ANSWERS — LEVEL 2

1. d

2. c The reaction is Finkelstein reaction.

3. (a) F^-; (b) I^-; (c) F^-; (d) $NH_2—NH_2$; (e) $CH_3SO_3^-$

4. (a) CH_3-Br (b) $CH_3-CH(Br)-CH_3$ (c) Fischer projection: Ph (top); H–C–Br; H–C–CH_3; Ph (bottom)

(d) Fischer projection: Ph (top); H–C–Br; Br–C–CH_3; Ph (bottom) (e) [1-bromotetralin: Br on the saturated ring]

5. (a) [cyclopentyl]–CH_2–Br (b) Ph–C(Br)(CH)–CH_2–CH_3 (c) [Br on cyclopentene ring] (d) [bicyclic ring with Cl on the bridge carbon] (e) [bicyclic ring with Cl on the ring]

6. a – p, w; b – q, x ; c – r, y; d – s, z

7. a – r, s; b – p, q; c – r, s; d – r, s

8. (a) [cyclopentyl]–CH_2CH_2–Br (b) $(CH_3)_3C-I$ (c)

9. (1) [zigzag chain]–Br (2) [zigzag chain]–I (3) [zigzag chain]–Cl

10. (X) A- reactants, B-transition state, C-Inter mediate, D- transition state

(Y) (i) exothermic (ii) B (iii) F (iv) a

11. A – b; B – b; C – d; D – a; E – b; F – b; G – b

12. A – c, d, e, f, h; B – b, c, f, i ; C – a, g, j

13.

Part –	1	2	3	4	5
Reaction–	A	D	E	G	I

14.

Yes –	a,	b,	c,	d,	f,	h,
No –	e,	g,	i,	j,	k	

15. a–p, q, r, s, t; b–p,s,t; c–p, q, r t; d–p

16. 2

17. a – p, r; b – q; c – s; d – r

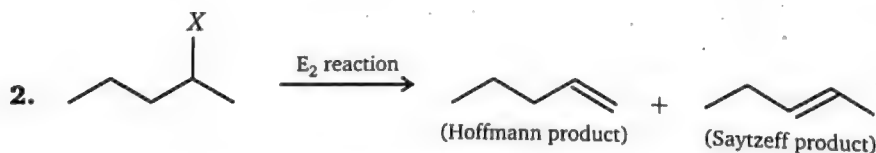
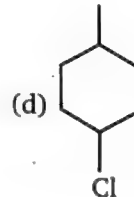
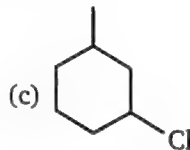
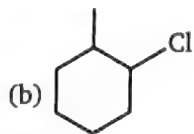
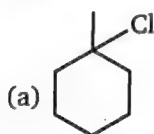
18. a – q; b – p; c – r; d – q

19. a – p; b – r; c – s; d – q

5B ALKYL HALIDES

Elimination Reactions (E_1, E_2, E_{1CB}, E_i)

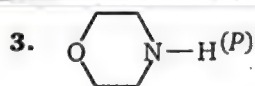
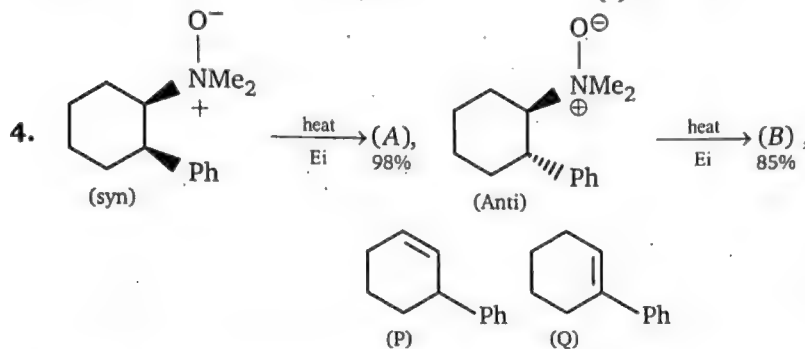
1. Which of the following alkyl halide gives only one product (excluding stereoisomer) when undergo E_2 reaction ?

   (E_2 = elimination bi-molecular)

(A) In the above reaction, maximum Saytzeff product will obtained when :

(a) $X = -I$ (b) $X = -Cl$ (c) $X = -Br$ (d) $X = -F$

(B) In the above reaction Hoffmann product is major when X is :

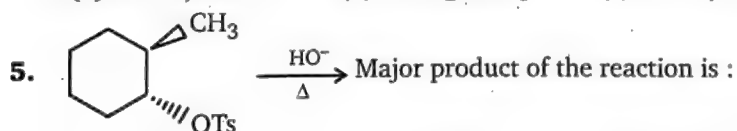
(a) –I (b) – Cl (c) – Br (d) – F

3. O N—H (P)

when (P) undergoes Hoffmann exhaustive methylation (twice) then the product obtained will be :

Product (A) & (B) of the above reaction is :

(a) $A = P, B = P$ (b) $A = Q, B = Q$ (c) $A = P, B = Q$ (d) $A = Q, B = P$

5.

Major product of the reaction is :

(a) (b) (c) (d)

6. Which of these dehydrates most easily ?

(a) $CH_3—CH_2—CH_2—OH$

(b) CH_3, —OH (cyclohexane ring)

(c) —OH (benzene ring)

(d) $CH_3—C(CH_3)_2—CH_2—OH$

7.

Product; Product of the reaction is :

(a)

(b)

(c)

(d) No reaction

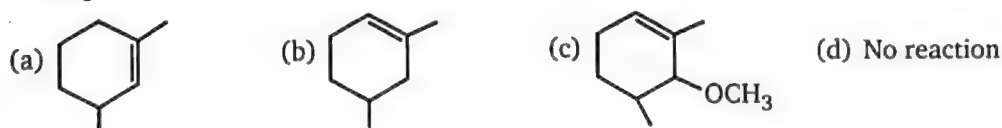
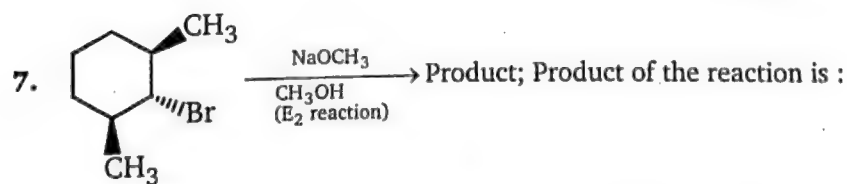
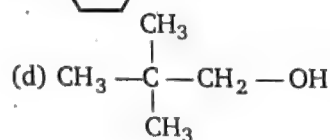
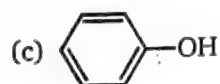
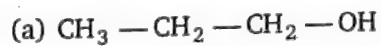
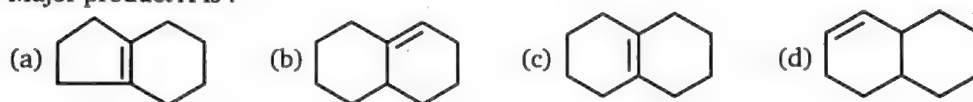
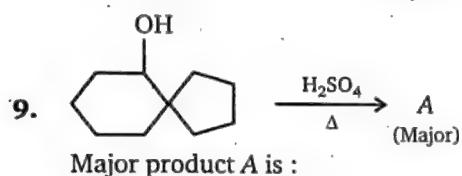
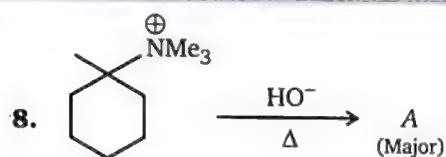
8.

Major product A is :

(a) (b) (c) (d)

9.

Major product A is :

(a) (b) (c) (d)

10. In which of the following reaction Saytzeff alkene is major product ?

(a) $CH_3-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\oplus}{N}Me_3 \xrightarrow[\Delta]{HO^-}$

(b) $CH_3-CH_2-CH_2-\underset{F}{CH}-CH_3 \xrightarrow[\Delta]{EtO^-}$

(c) $CH_3-CH_2-\underset{Br}{\overset{CH_3}{C}}-CH_3 \xrightarrow[\Delta]{t\text{-}BuOK}$

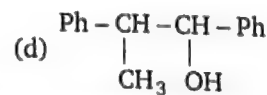
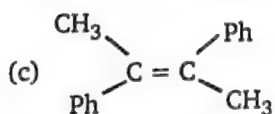
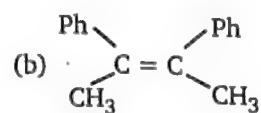
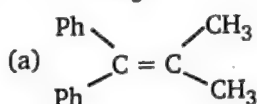
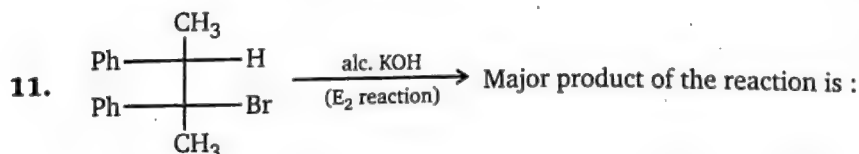
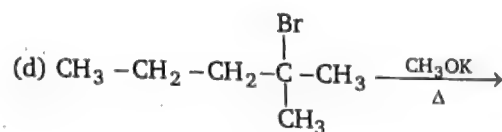
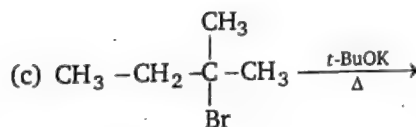
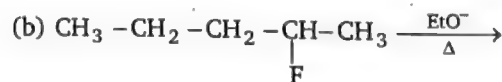
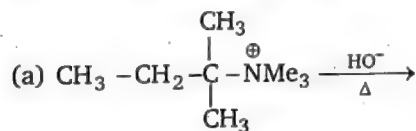
(d) $CH_3-CH_2-CH_2-\underset{CH_3}{\overset{Br}{C}}-CH_3 \xrightarrow[\Delta]{CH_3OK}$

11. Fischer projection: top CH_3; Ph—C—H; Ph—C—Br; bottom CH_3 $\xrightarrow[(E_2 \text{ reaction})]{\text{alc. KOH}}$ Major product of the reaction is :

(a) $(Ph)(Ph)C=C(CH_3)(CH_3)$

(b) $(Ph)(CH_3)C=C(Ph)(CH_3)$ [Ph on top of both carbons]

(c) $(CH_3)(Ph)C=C(Ph)(CH_3)$ [CH_3 top-left, Ph top-right]

(d) $Ph-\underset{CH_3}{CH}-\underset{OH}{CH}-Ph$

12. The conversion of 2, 3-dibromobutane to 2-butene with Zn is :

(a) Redox reaction

(b) α-Elimination

(c) β-Elimination

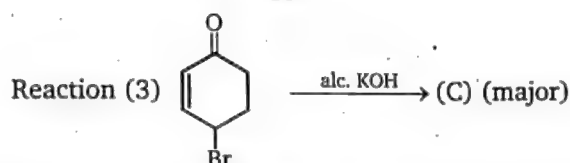
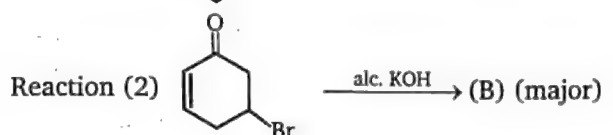
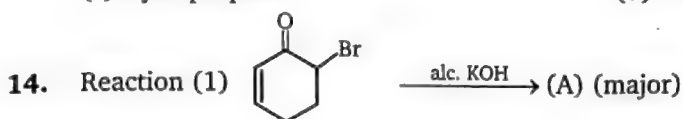
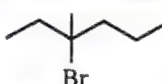
(d) Both α-elimination and redox reaction

13. 1, 3-Dibromopropane is heated with zinc dust in ether. The product formed is :

(a) propene (b) propane
(c) cyclopropane (d) 3-bromopropane

14. Reaction (1) $\xrightarrow{\text{alc. KOH}}$ (A) (major)

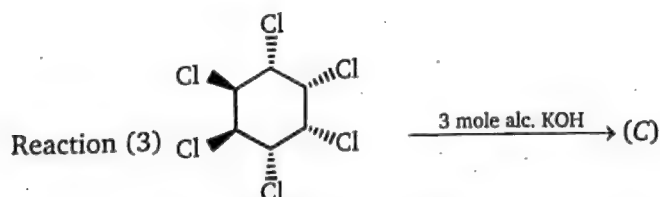
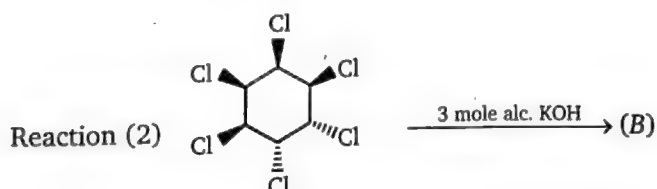
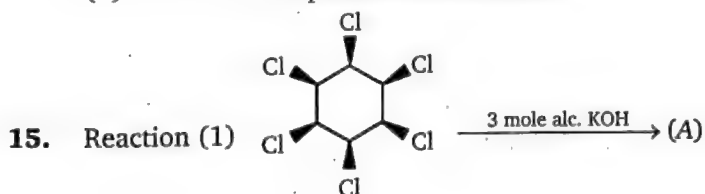
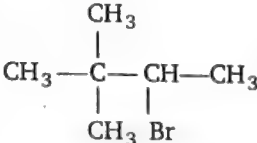
Reaction (2) $\xrightarrow{\text{alc. KOH}}$ (B) (major)

Reaction (3) $\xrightarrow{\text{alc. KOH}}$ (C) (major)

Product obtained in above reactions (1), (2) & (3) is :

(a) A = B but C is different
(b) A = C, but B is different
(c) B = C, but A is different
(d) A = B = C all product are identical

15. Reaction (1) $\xrightarrow{\text{3 mole alc. KOH}}$ (A)

Reaction (2) $\xrightarrow{\text{3 mole alc. KOH}}$ (B)

Reaction (3) $\xrightarrow{\text{3 mole alc. KOH}}$ (C)

Product obtained in above reactions (1), (2) & (3) is :

(a) $A = B$, C is different (b) $A = C$, B is different
(c) $B = C$, A is different (d) $A = B = C$ is same

16. [skeletal structure with Br] $\xrightarrow{\text{alc. KOH}}$ (x)

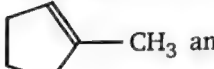
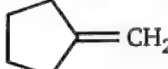
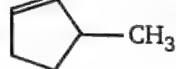
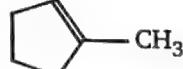
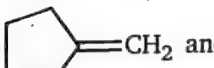
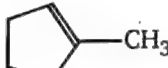
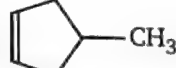
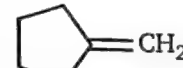
x is number of E_2 product obtained (including stereoisomers)

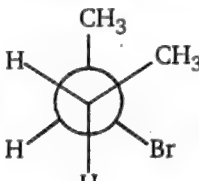
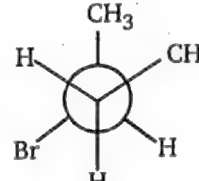
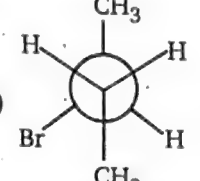
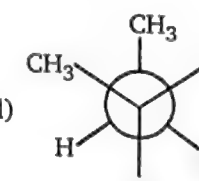
Find (x).

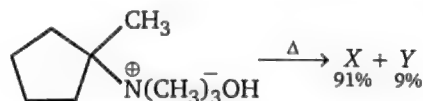
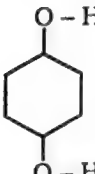
(a) 3 (b) 4 (c) 5 (d) 6

17. $CH_3-C(CH_3)_2-CH(Br)-CH_3 \xrightarrow[\Delta]{\text{EtOH}} (A)$

Major product (A) is :

(a) (b) (c) (d) [structures]

18. Which one of the following compound will be least susceptible to elimination of hydrogen bromide ?

(a) $Br-CH_2-CH_2-NO_2$ (b) $Br-CH_2-CH_2-CH_3$
(c) $Br-CH_2-CH_2-CN$ (d) $Br-CH_2-CH_2-CO_2Et$

19. Two alkenes, X(91% yield) and Y(9% yield) are formed when the following compound is heated.

[1-methylcyclopentyl with $\overset{\oplus}{N}(CH_3)_3\overline{O}H$] $\xrightarrow{\Delta}$ $X + Y$ (91% 9%)

The structures of X and Y, respectively are :

(a) [ring]$-CH_3$ and [ring]$=CH_2$ (b) [ring]$-CH_3$ and [ring]$-CH_3$

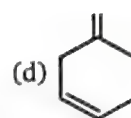
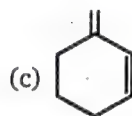
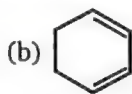
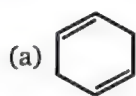
(c) [ring]$=CH_2$ and [ring]$-CH_3$ (d) [ring]$-CH_3$ and [ring]$=CH_2$

20. In the dehydrohalogenation of 2-bromobutane; which conformation leads to the formation of *cis*-2-butene ?

(a) (b) (c) (d) [Newman projections]

21. [cyclohexane-1,4-diol, O–H, O–H] $\xrightarrow[\text{Pyridine}]{CH_3-\overset{O}{\overset{\|}{C}}-Cl \text{ (2 mole)}}$ (A) $\xrightarrow[\Delta]{\text{(Ei)}}$ (B) + CH_3CO_2H

Product (*B*) of given reaction is:

(a)   (b)   (c)   (d)

22. What product will be formed from Hoffmann exhaustive methylation of following compound?

$$Me_2CHCH_2NHCH_2CH_2Me \xrightarrow[\text{(ii) } Ag_2O \text{ (iii) } \Delta]{\text{(i) } CH_3-I \text{ (excess)}} \text{Product}$$

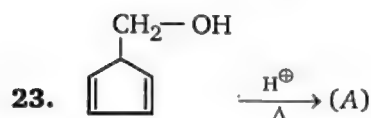
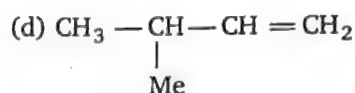
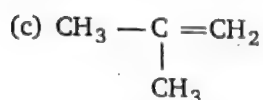
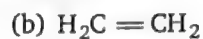
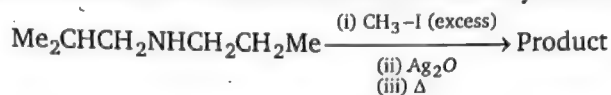
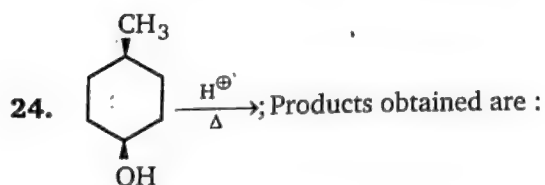
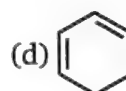
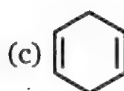
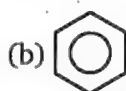
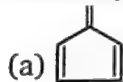
(a) $Me-CH=CH_2$ (b) $H_2C=CH_2$

(c) $CH_3-C(CH_3)=CH_2$ (d) $CH_3-CH(Me)-CH=CH_2$

23. CH_2-OH $\xrightarrow[\Delta]{H^{\oplus}}$ (*A*)

Product (*A*) is :

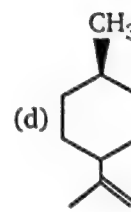
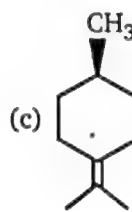
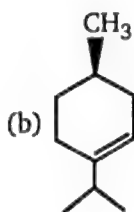
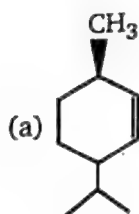
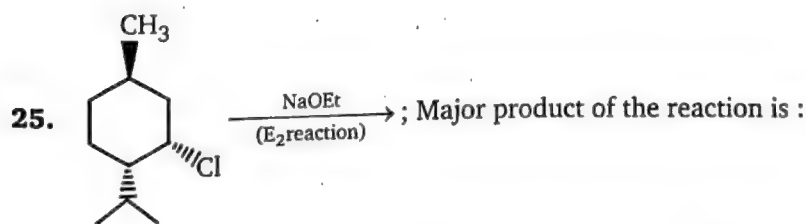
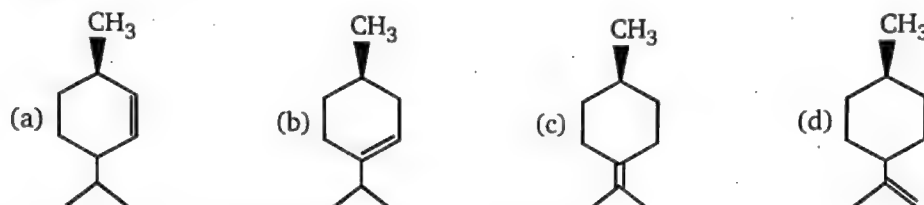
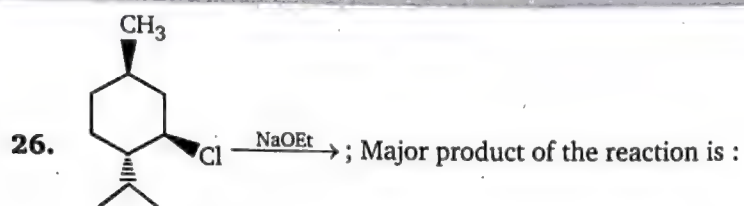
(a)   (b)   (c)   (d)

24. CH_3 / OH $\xrightarrow[\Delta]{H^{\oplus}}$; Products obtained are :

(a) Racemic (b) Diastereomers (c) G.I (d) Positional isomers

25.

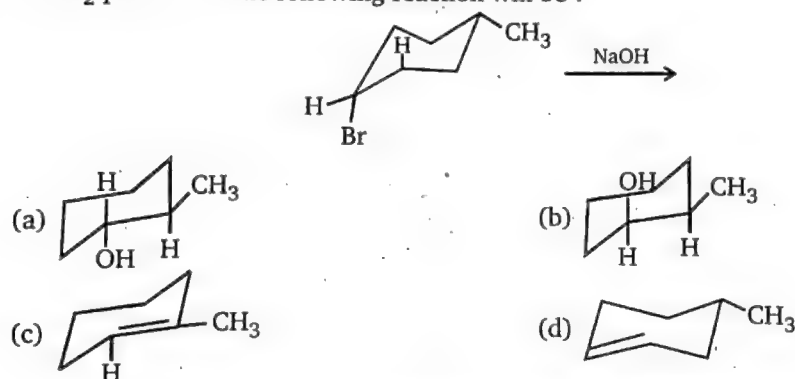
(a)   (b)   (c)   (d)

26. $\xrightarrow{NaOEt}$; Major product of the reaction is :

(a) (b) (c) (d)

27. The E_2 product of the following reaction will be ?

(a) (c)

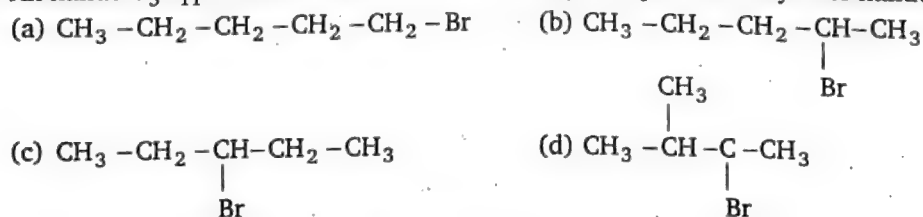
(b)

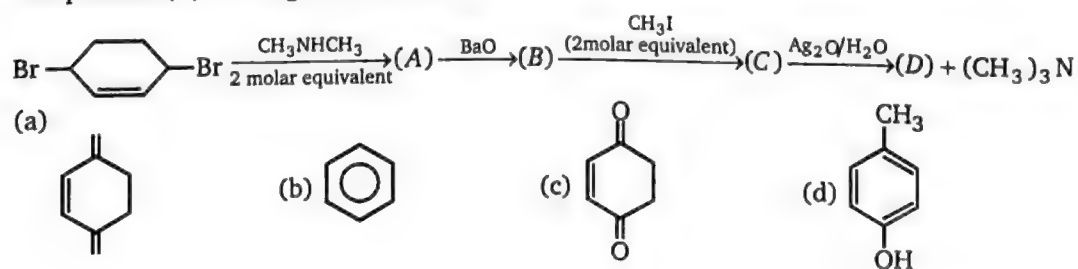
(d)

28. An halide $C_5H_{11}Br$ on treatment with alc. KOH give 2-pentene only. The halide will be :

(a) $CH_3-CH_2-CH_2-CH_2-CH_2-Br$

(b) $CH_3-CH_2-CH_2-CH(Br)-CH_3$

(c) $CH_3-CH_2-CH(Br)-CH_2-CH_3$

(d) $CH_3-CH(CH_3)-C(Br)-CH_3$

29. End product (D) in the given sequence is:

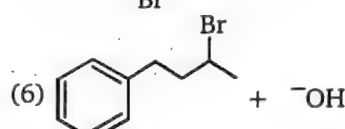
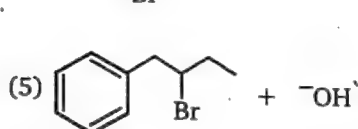
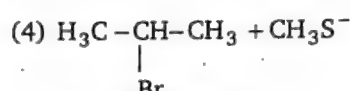
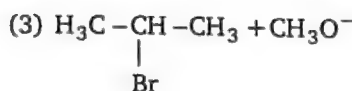
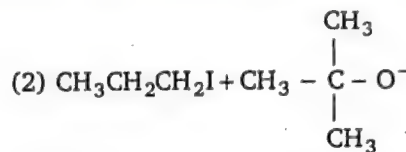
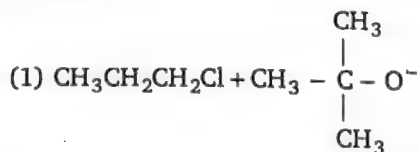
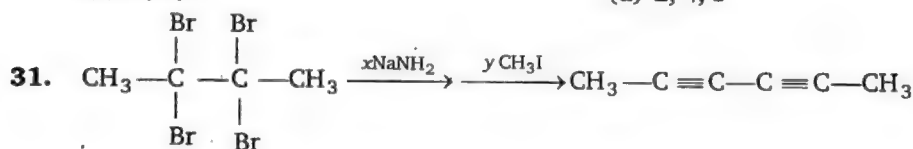
(a) (b) (c) (d)

30. For each of the following pairs of E_2 reaction, select the one that occurs with the greater rate constant.

(1) $CH_3CH_2CH_2Cl + CH_3-C(CH_3)_2-O^-$ (2) $CH_3CH_2CH_2I + CH_3-C(CH_3)_2-O^-$

(3) $H_3C-CH(Br)-CH_3 + CH_3O^-$ (4) $H_3C-CH(Br)-CH_3 + CH_3S^-$

(5) $C_6H_5CH_2CH(Br)CH_2CH_3 + {}^-OH$ (6) $C_6H_5CH_2CH_2CH(Br)CH_3 + {}^-OH$

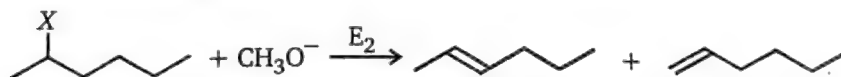
(a) 2, 4, 6 (b) 1, 3, 5
(c) 2, 3, 5 (d) 2, 4, 5

31. $CH_3-CBr_2-CBr_2-CH_3 \xrightarrow{x\,NaNH_2} \xrightarrow{y\,CH_3I} CH_3-C\equiv C-C\equiv C-CH_3$

x and y mole consumed.

Value of $x + y$ =

(a) 5 (b) 6 (c) 7 (d) 8

32. The following bimolecular elimination reaction (E_2) is carried out with different halogen leaving groups. The per cent yield of the two products (2-hexene and 1-hexene) for each leaving group is listed below.

2-X-hexane $+ CH_3O^- \xrightarrow{E_2}$ 2-hexene + 1-hexene

Leaving group	Conj. Acid pK_a	%-yield of 2-hexene	%-yield of 1-hexene
$X = I$	−10	81%	19%
$X = Br$	−9	72%	28%
$X = Cl$	−7	67%	33%
$X = F$	3.2	30%	70%

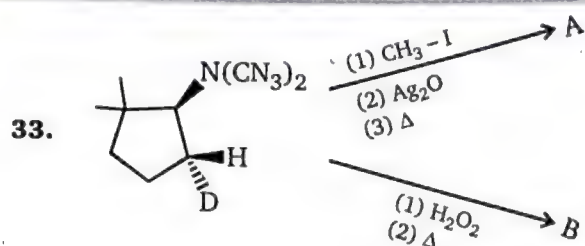
Which of the following statement is (are) true concerning this series of E_2 reactions ?

(a) Based on the pK_a's of the conjugate acid, I^- is the best leaving group and F^- is the poorest leaving group

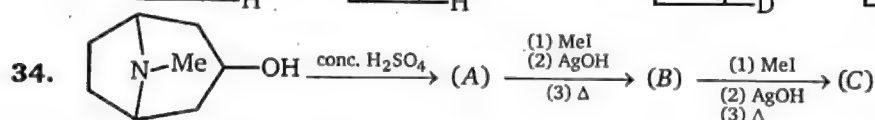
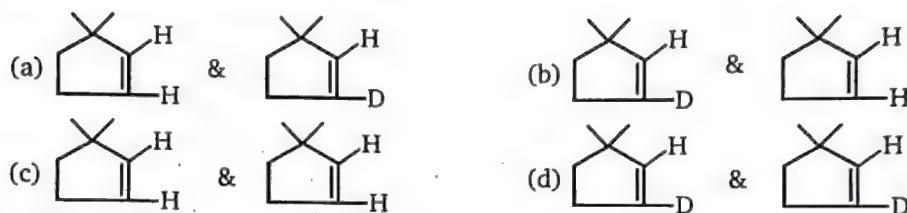
(b) When I^-, Br^- and Cl^- are used as leaving groups, Zaitsev's rule is followed

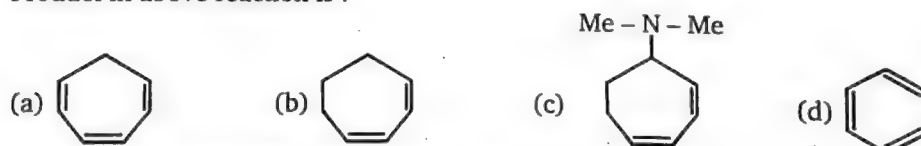
(c) F^- is the strongest base (and therefore the poorest leaving group) and the transition state for reaction with fluoride as the leaving group has the least double bond character

(d) a, b, c are true

33.

Product (A) & (B) respectively are :

(a) & (b) & (c) & (d) &

34.

Product in above reaction is :

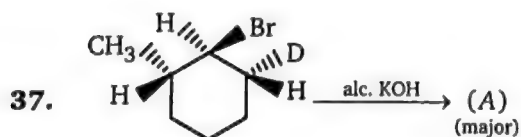
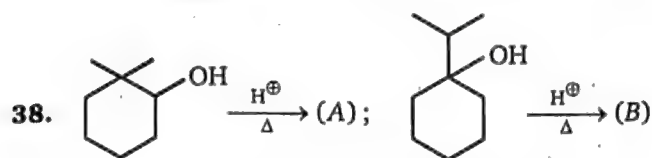
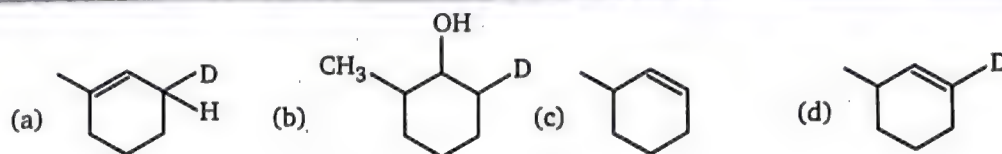
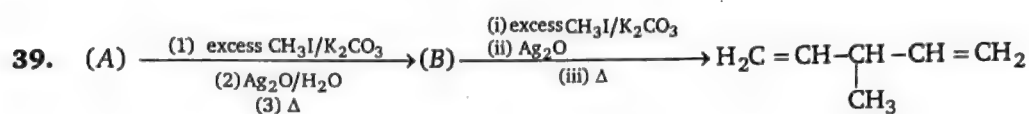
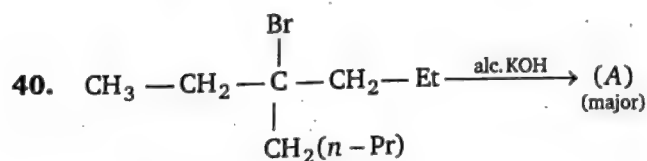
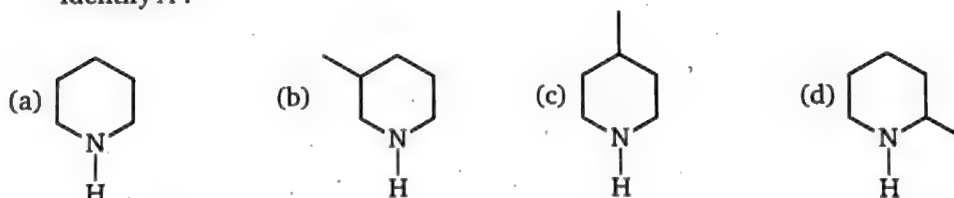
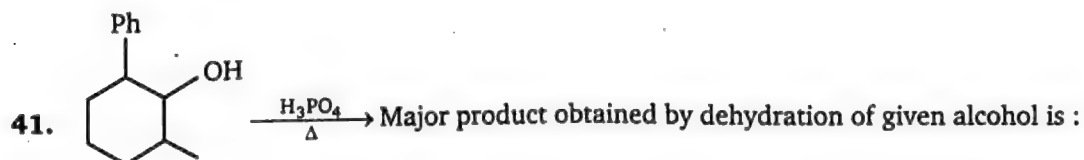
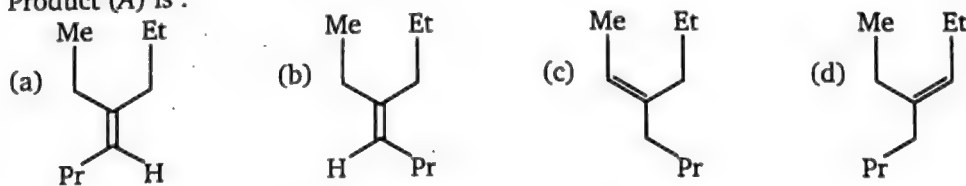
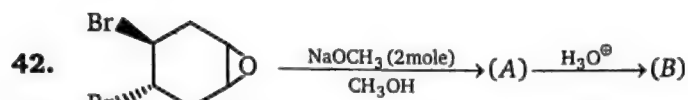
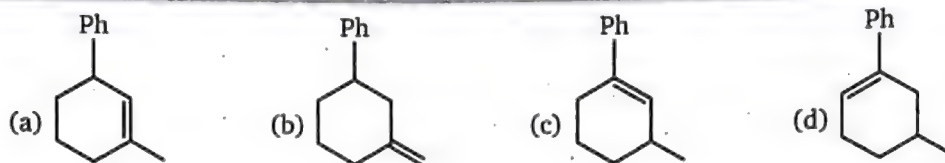
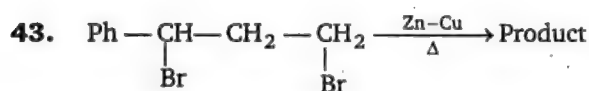
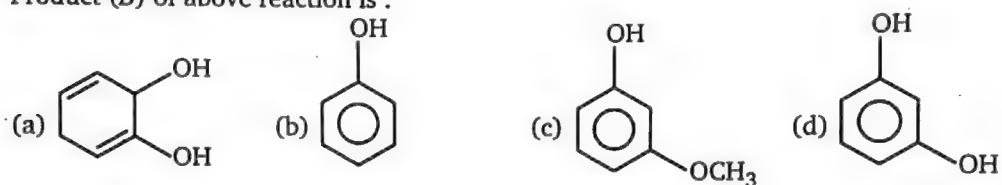
(a) (b) (c) Me – N – Me (d)

35. Major product obtained in the reaction of 1-phenyl-2-bromobutane with NaOMe is :
(a) (E)-1-phenylbut-1-ene
(b) (E)-1-phenylbut-2-ene
(c) 1-phenyl-2-ethoxybutane
(d) (Z)-1-phenylbut-2-ene

36. Which of the following alkyl halides give most complex mixture of alkene in an E_2 reaction ?
(a) $CH_3-CH_2-CH_2-CH_2-Br$
(b) $CH_3-CH_2-CH_2-CH(Br)-CH_3$
(c) $CH_3-CH_2-CH(Br)-CH_2-CH_3$
(d) $CH_3-C(CH_3)(Br)-CH_2-CH_3$

37.

Product (A) is :

(a) (b) (c) (d)

38. $\xrightarrow[\Delta]{H^{\oplus}}$ (A) ; $\xrightarrow[\Delta]{H^{\oplus}}$ (B)

Sum of number of α-hydrogen present is compound $A + B$ is :
(a) 18 (b) 19 (c) 20 (d) 21

39. $(A) \xrightarrow[\text{(2) } Ag_2O/H_2O \text{ (3) } \Delta]{\text{(1) excess } CH_3I/K_2CO_3} (B) \xrightarrow[\text{(iii) } \Delta]{\text{(i) excess } CH_3I/K_2CO_3 \text{ (ii) } Ag_2O} H_2C=CH-CH(CH_3)-CH=CH_2$

Identify A :

(a) (b) (c) (d)

40. $CH_3-CH_2-C(Br)(CH_2(n-Pr))-CH_2-Et \xrightarrow{\text{alc. KOH}} (A)$ (major)

n - Pr = n - propyl

Product (A) is :

41. $\xrightarrow[\Delta]{H_3PO_4}$ Major product obtained by dehydration of given alcohol is :

(a) Ph (b) Ph (c) Ph (d) Ph

42. $\xrightarrow[CH_3OH]{NaOCH_3\text{ (2mole)}} (A) \xrightarrow{H_3O^{\oplus}} (B)$

Product (*B*) of above reaction is :

(a) OH, OH (b) OH (c) OH, OCH_3 (d) OH, OH

43. $Ph-\underset{Br}{CH}-CH_2-\underset{Br}{CH_2} \xrightarrow[\Delta]{Zn-Cu}$ Product

Product of the above reaction is :

(a) $Ph-CH=CH-CH_2-Br$ (b) Ph–cyclopropyl
(c) $PH-\dot{C}HBr-CH=CH_2$ (d) $Ph-C\equiv C-CH_3$

44. OH, OH $\xrightarrow[\Delta]{H^{\oplus}} (A)$

Product (*A*) is :

(a) (b) (c) (d)

45. H, Ph, H, Me, Ph, $\overset{\oplus}{N}Me_3$ $\xrightarrow[\Delta]{NaOEt}$

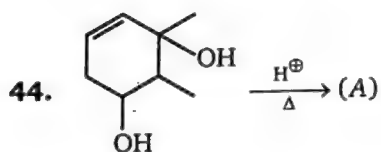
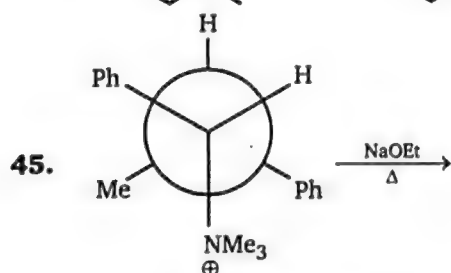
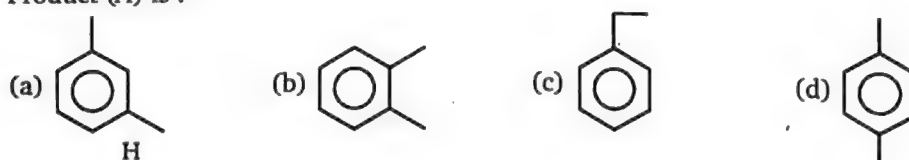
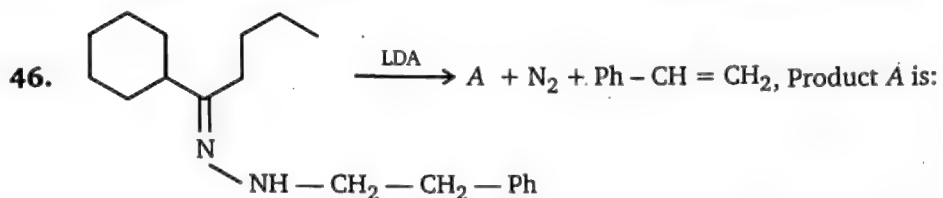
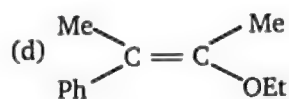
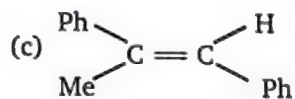
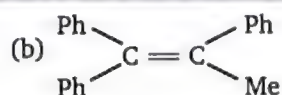
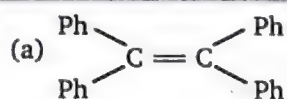
Major product of the above reaction is :

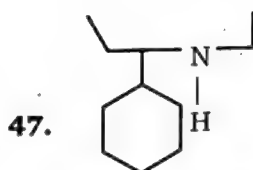
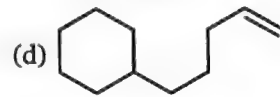
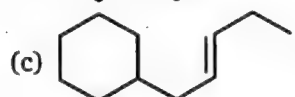
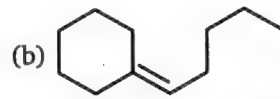
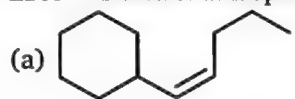
(a) $Ph_2C=CPh_2$ (b) $Ph_2C=C(Ph)Me$

(c) $Ph(Me)C=CH(Ph)$ (d) $Me(Ph)C=C(Me)OEt$

46. $\xrightarrow{\text{LDA}} A + N_2 + Ph-CH=CH_2$, Product A is:

N

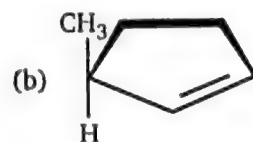
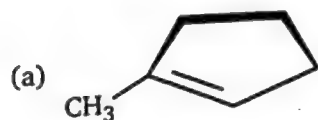
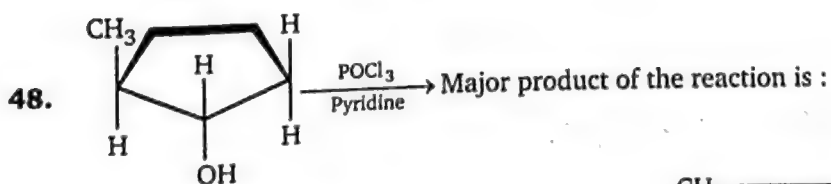
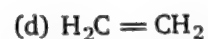
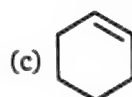
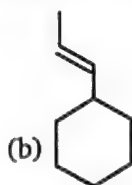
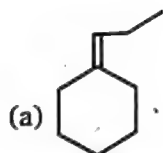
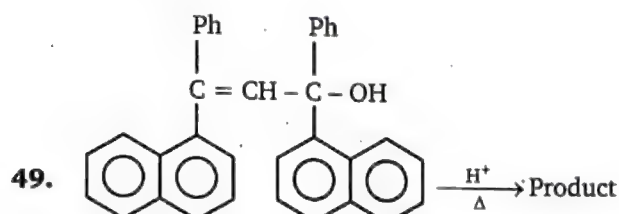
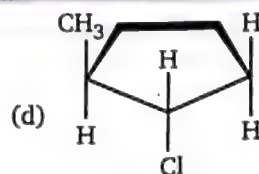
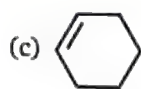
$NH-CH_2-CH_2-Ph$

LDA = Lithium di-isopropyl amide

47.

Major product of the reaction, when the given compound undergoes Hoffmann exhaustive methylation is :

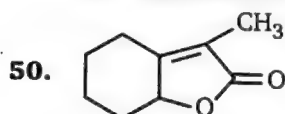
(d) $H_2C=CH_2$

48.

(c) (d)

49. $\xrightarrow[\Delta]{H^+}$ Product

Stereochemistry of the product is :

(a) Meso compound
(b) Racemic mixture
(c) Diastereomer
(d) Optically pure enantiomers

50. CH_3 =O O

Which of the following reactant is used to obtain above compound (*A*). (Assume that EtO^- is used in all the reaction)

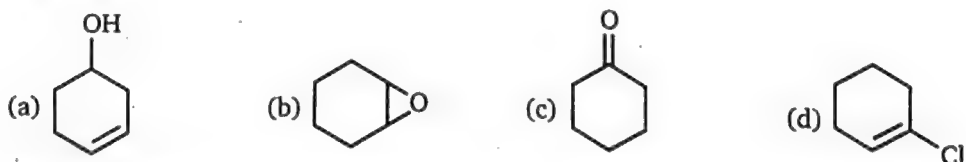
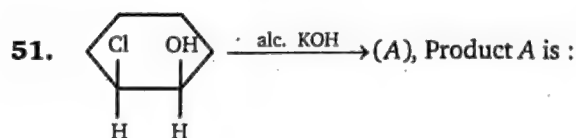
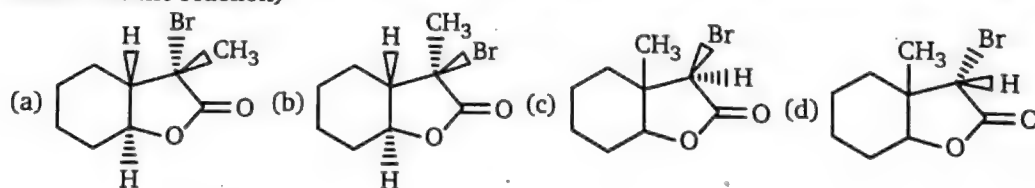
(a) H Br CH_3 =O O H
(b) H CH_3 Br =O O H
(c) CH_3 Br H =O O
(d) CH_3 Br H =O O

51. Cl OH H H $\xrightarrow{\text{alc. KOH}}$ (*A*), Product *A* is :

(a)

(b) O

(c)

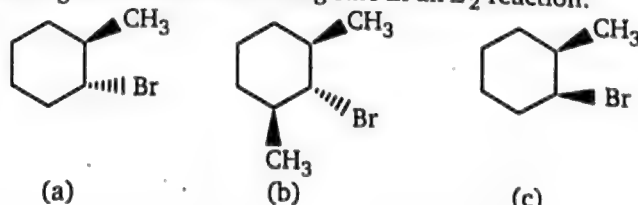
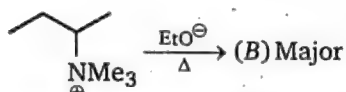
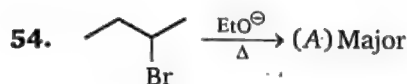
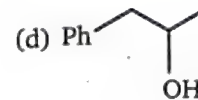
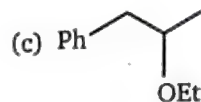
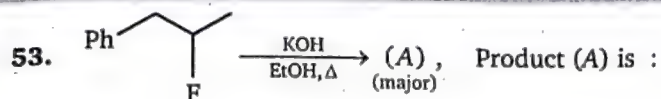
(d) Cl

52. Rank the following in order of decreasing rate in an E_2 reaction:

(a) a > b > c
(b) c > a > b
(c) c > b > a
(d) b > a > c

53. Ph–CH₂–CH(F)–CH₃ $\xrightarrow[\text{EtOH}, \Delta]{\text{KOH}}$ (A) (major), Product (A) is :

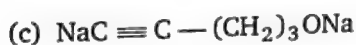
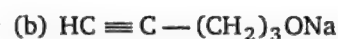
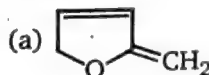
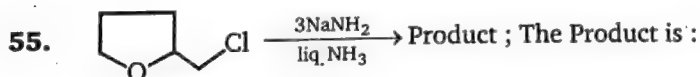
(a) Ph–CH₂–CH=CH₂ (b) Ph–CH=CH–CH₃ (c) Ph–CH₂–CH(OEt)–CH₃ (d) Ph–CH₂–CH(OH)–CH₃

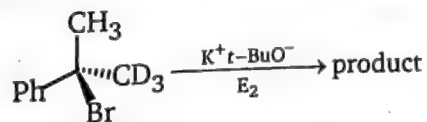
54. $CH_3CH_2CH(Br)CH_3 \xrightarrow[\Delta]{EtO^{\ominus}}$ (A) Major

$CH_3CH_2CH(\overset{\oplus}{N}Me_3)CH_3 \xrightarrow[\Delta]{EtO^{\ominus}}$ (B) Major

Relation between (A) and (B) is :

(a) G.I.
(b) Positional isomer
(c) Enantiomer
(d) Chain isomer

55. (Tetrahydrofuran-2-yl)methyl chloride $\xrightarrow[\text{liq. } NH_3]{3NaNH_2}$ Product ; The Product is :

(a) 2-methylene-2,3-dihydrofuran (ring with =CH₂)
(b) $HC \equiv C-(CH_2)_3ONa$
(c) $NaC \equiv C-(CH_2)_3ONa$
(d) $H-C \equiv C-(CH_2)_3OH$

56. Which best describes the product of the following reaction ?

Ph–C(CH₃)(CD₃)(Br) $\xrightarrow[E_2]{K^+ t\text{-BuO}^-}$ product

(a) Absolute configuration has been inverted
(b) Absolute configuration has been retained
(c) Racemization (loss of absolute configuration) has occurred
(d) Loss of chirality has occurred (the product is achiral)

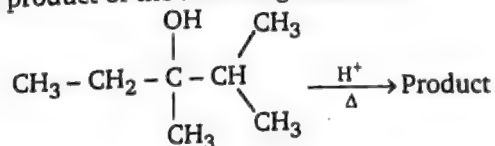
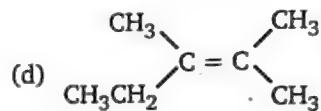
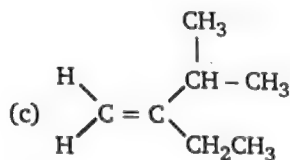
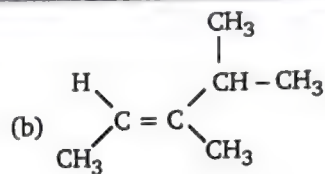
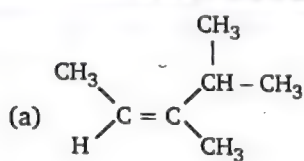
57. What is the major product of the following reaction ?

$CH_3-CH_2-C(OH)(CH_3)-CH(CH_3)_2 \xrightarrow[\Delta]{H^+}$ Product

(a) $(CH_3)(H)C=C(CH_3)(CH(CH_3)CH_3)$

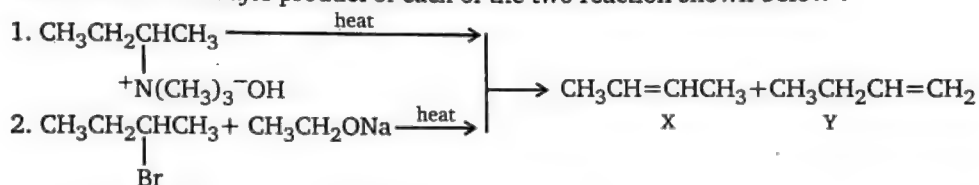
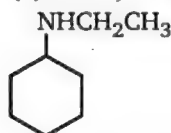
(b) $(H)(CH_3)C=C(CH_3)(CH(CH_3)CH_3)$

(c) $(H)(H)C=C(CH_2CH_3)(CH(CH_3)CH_3)$

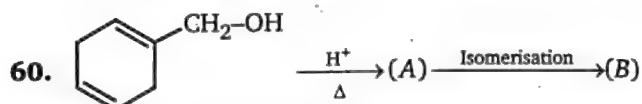
(d) $(CH_3)(CH_3CH_2)C=C(CH_3)(CH_3)$

58. What will be the major product of each of the two reaction shown below ?

1. $CH_3CH_2CH(N^+(CH_3)_3\,^-OH)CH_3 \xrightarrow{heat}$

2. $CH_3CH_2CH(Br)CH_3 + CH_3CH_2ONa \xrightarrow{heat}$

$\longrightarrow \underset{X}{CH_3CH{=}CHCH_3} + \underset{Y}{CH_3CH_2CH{=}CH_2}$

(a) 1 – X, 2 – X (b) 1 – Y, 2 – X (c) 1 – X, 2 – Y (d) 1 – Y, 2 – Y

59. (cyclohexyl-$NHCH_2CH_3$) + CH_3I (excess) $\longrightarrow$ product; The product is :

(a) a primary amine
(b) a tertiary amine
(c) a secondary amine
(d) a quaternary ammonium salt

60. (cyclohexadiene with $CH_2–OH$) $\xrightarrow[\Delta]{H^+}$ (A) $\xrightarrow{\text{Isomerisation}}$ (B)

(A) on heating isomerizes to (B). What is the structure of (B) ?

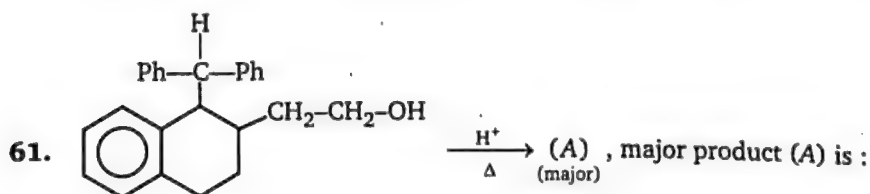
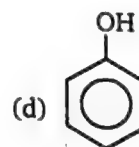
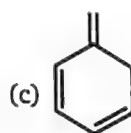
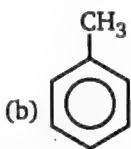
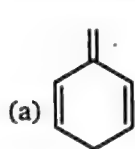
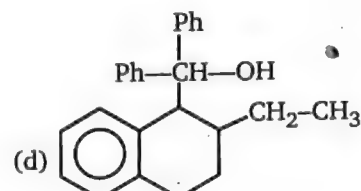
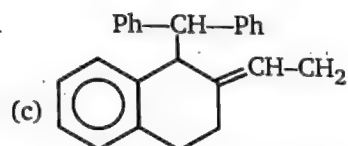
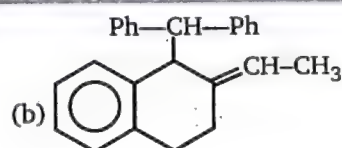
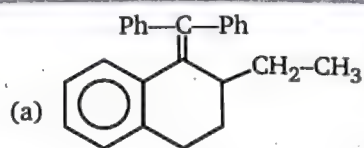
(a) (methylenecyclohexadiene) (b) (toluene, CH_3) (c) (methylenecyclohexadiene) (d) (phenol, OH)

61. (tetralin bearing $Ph–C(H)–Ph$ and $CH_2–CH_2–OH$) $\xrightarrow[\Delta]{H^+}$ $\underset{\text{(major)}}{(A)}$, major product (A) is :

(a) Ph—C—Ph, CH_2-CH_3

(b) Ph—CH—Ph, $CH-CH_3$

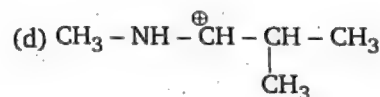
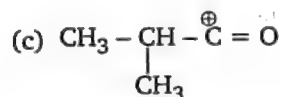
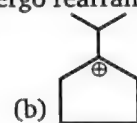
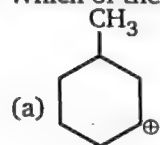
(c) Ph—CH—Ph, $CH-CH_2$

(d) Ph, Ph—CH—OH, CH_2-CH_3

62. Which of the following carbocation will undergo rearrangement ?

(a) CH_3 ⊕

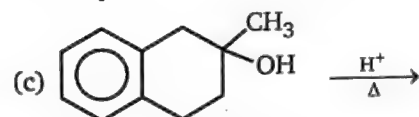
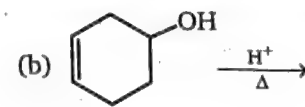
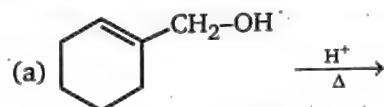
(b) ⊕

(c) $CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{\oplus}{C}=O$

(d) $CH_3-NH-\overset{\oplus}{CH}-\underset{CH_3}{\underset{|}{CH}}-CH_3$

63. In which of the following reaction resonance stabilized product will form ?

(a)

(b) OH $\xrightarrow[\Delta]{H^+}$

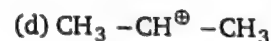
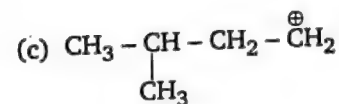
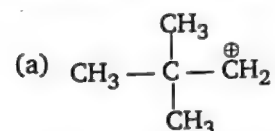
(c) CH_3, OH $\xrightarrow[\Delta]{H^+}$

(d) All of these

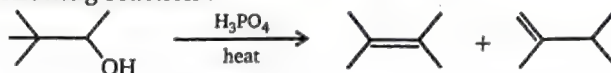
64. In which of following reaction rearrangement take place with change in carbon skeleton ?

(a) $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\oplus}{C}H_2$

(b) $CH_3-CH_2CH_2^{\oplus}$

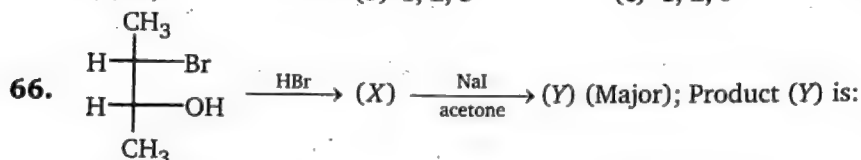
(c) $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{\oplus}{C}H_2$

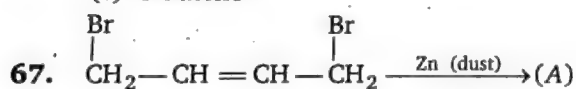
(d) $CH_3-CH^{\oplus}-CH_3$

65. Consider the following reaction :

$\xrightarrow[\text{heat}]{H_3PO_4}$ (OH) +

Which response contains all the correct statement about this process ?

(1) Dehydration
(2) E_2 mechanism
(3) Carbon skeleton migration
(4) Most stable alkene will form
(5) Single-step reaction

(a) 1, 3 (b) 1, 2, 3 (c) 1, 2, 5 (d) 1, 3, 4

66.

(a) *cis*-2-butene
(b) *trans*-2-butene
(c) 1-butene
(d) Iso-butene

67. $\underset{\displaystyle Br}{CH_2}-CH=CH-\underset{\displaystyle Br}{CH_2} \xrightarrow{\text{Zn (dust)}} (A)$

Above reaction is an example of 1,4-elimination. Predict the product.

(a) $CH_3-CH=C=CH_2$
(b) $CH_3-C\equiv C-CH_3$
(c) $CH_3-CH_2-C\equiv CH$
(d) $H_2C=CH-CH=CH_2$

68. (Ph, OH, Ph, Ph) $\xrightarrow{\text{conc. } H_2SO_4}$ Major product of the reaction is:

(a)

(b)

(c)

(d) None of these

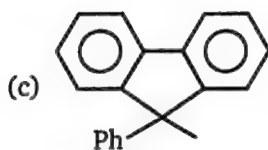
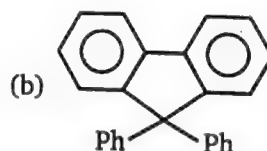
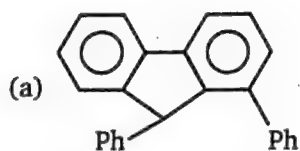
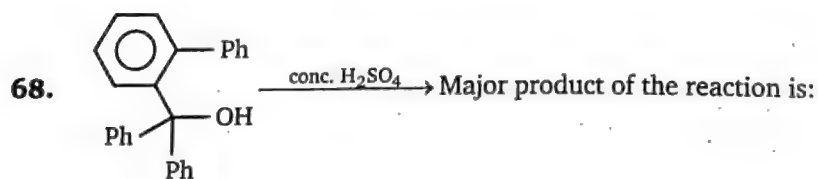
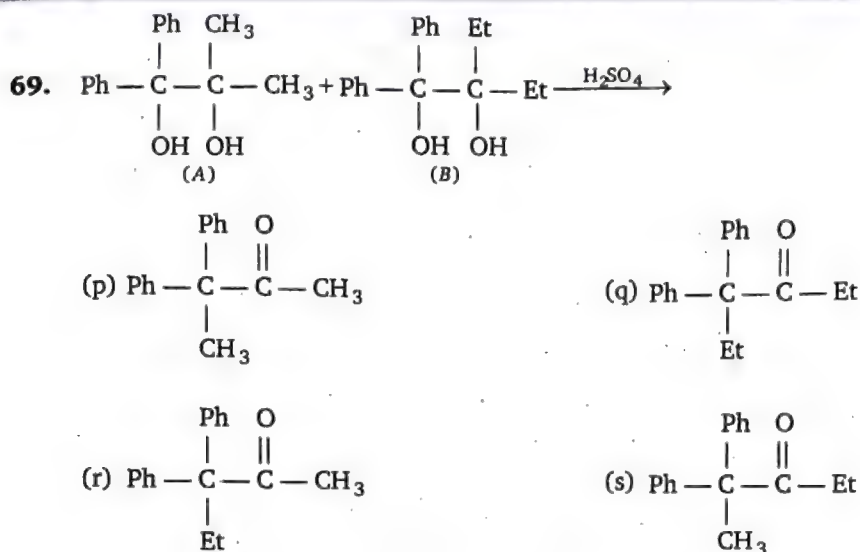
69. $Ph-C(Ph)(OH)-C(CH_3)(OH)-CH_3 + Ph-C(Ph)(OH)-C(Et)(OH)-Et \xrightarrow{H_2SO_4}$

(A) (B)

(p) $Ph-C(Ph)(CH_3)-C(=O)-CH_3$

(q) $Ph-C(Ph)(Et)-C(=O)-Et$

(r) $Ph-C(Ph)(Et)-C(=O)-CH_3$

(s) $Ph-C(Ph)(CH_3)-C(=O)-Et$

When (A) and (B) reacts with H_2SO_4 products obtained are :

(a) p, q, r, s (b) p, q (c) p, q, r (d) p, q, s

70. Which of the following compound gives even number of Hoffmann's exhaustive methylation and elimination?

(a)

(b)

(c) N

(d) NH

71. CH_3, I, CH_2, CH_3, $CH-CH_3$, CH_3 $\xrightarrow{\text{alc.KOH}}$ X = Number of chiral products (including stereoisomer).

(a) 2 (b) 4 (c) 6 (d) 8

72. Cl, O $\xrightarrow[t\text{-butO}]{t\text{-butO}^{\ominus}}$ (A) ; "(A)" is :

(a) t-but O (b) $O^{\ominus}$

(c) (d) Cl, O t-but

O O O

73. $\xrightarrow{\text{Conc. } H_2SO_4}$ $A + H_2O$ (Major)

OH

which of the following is product "A" in the above reaction?

(a) (b)

(c) (d)

ANSWERS — LEVEL 1															
1.	(d)	**2.**	A – a B – d	**3.**	(a)	**4.**	(c)	**5.**	(b)	**6.**	(b)	**7.**	(d)	**8.**	(b)
9.	(c)	**10.**	(d)	**11.**	(c)	**12.**	(c)	**13.**	(c)	**14.**	(d)	**15.**	(d)	**16.**	(c)
17.	(b)	**18.**	(b)	**19.**	(c)	**20.**	(a)	**21.**	(b)	**22.**	(a)	**23.**	(b)	**24.**	(a)
25.	(b)	**26.**	(a)	**27.**	(d)	**28.**	(c)	**29.**	(b)	**30.**	(c)	**31.**	(d)	**32.**	(d)
33.	(a)	**34.**	(a)	**35.**	(a)	**36.**	(b)	**37.**	(c)	**38.**	(c)	**39.**	(c)	**40.**	(c)
41.	(c)	**42.**	(b)	**43.**	(b)	**44.**	(b)	**45.**	(c)	**46.**	(a)	**47.**	(d)	**48.**	(b)
49.	(b)	**50.**	(a)	**51.**	(c)	**52.**	(b)	**53.**	(b)	**54.**	(b)	**55.**	(c)	**56.**	(d)
57.	(d)	**58.**	(b)	**59.**	(d)	**60.**	(b)	**61.**	(a)	**62.**	(b)	**63.**	(d)	**64.**	(a)
65.	(d)	**66.**	(b)	**67.**	(d)	**68.**	(b)	**69.**	(b)	**70.**	(a,b)	**71.**	(b)	**72.**	(b)
73.	(a)														

1. Comprehension

E_2 reaction → Elimination bimolecular

In the general mechanism of the E_2 reaction a strong base abstract a proton on a carbon atom adjacent to the one of the leaving group. As the base abstracts a proton, a double bond forms and the leaving group leaves.

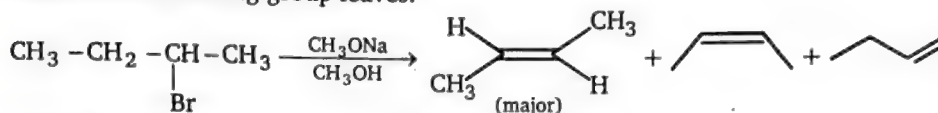
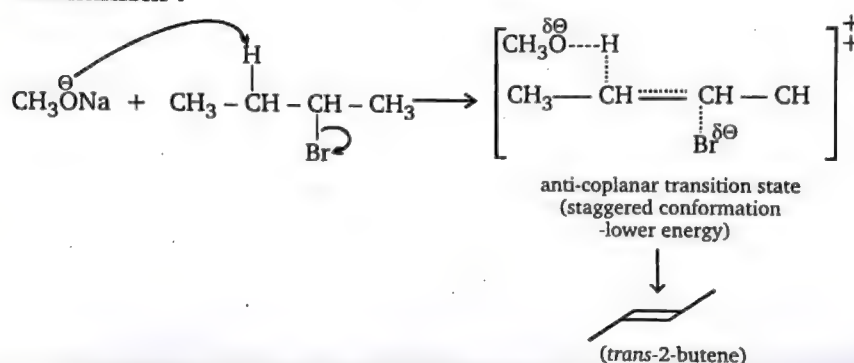
$CH_3-CH_2-CH(Br)-CH_3 \xrightarrow[CH_3OH]{CH_3ONa}$ (H)(CH$_3$)C=C(CH$_3$)(H) (major) + [cis-2-butene] + [1-butene]

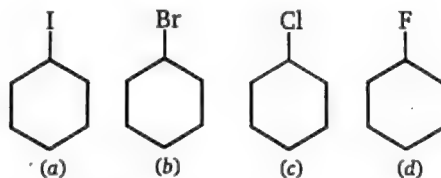
Mechanism :

$CH_3\overset{\ominus}{O}Na + CH_3-CH(H)-CH(Br)-CH_3 \longrightarrow \left[\begin{array}{c} CH_3\overset{\delta\ominus}{O}\text{----}H \\ CH_3\text{—}CH\text{.....}CH\text{—}CH \\ Br^{\delta\ominus} \end{array}\right]^{\ddagger}$

anti-coplanar transition state
(staggered conformation
-lower energy)

↓

(*trans*-2-butene)

A. Identify the rate of reaction of given compounds in E_2 reaction:

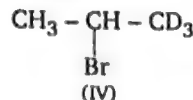
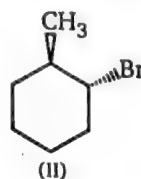
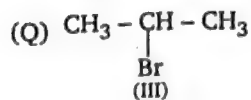
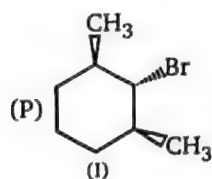
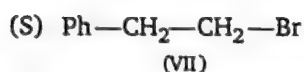
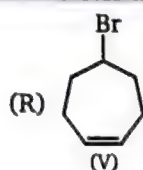
(a) iodocyclohexane (b) bromocyclohexane (c) chlorocyclohexane (d) fluorocyclohexane

(a) $a > b > c > d$ (b) $a > c > b > d$ (c) $b > a > c > d$ (d) $b > d > a > c$

B. In given pairs, which compound is more reactive toward E_2 reaction:

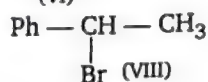
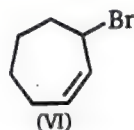
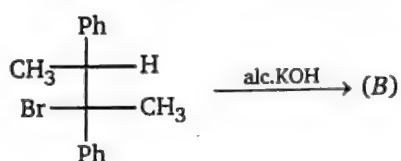
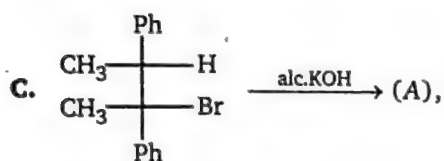
(P) (I) [cyclohexane with CH$_3$, Br, CH$_3$] (II) [cyclohexane with CH$_3$, Br]

(Q) $CH_3-CH(Br)-CH_3$ (III) $CH_3-CH(Br)-CD_3$ (IV)

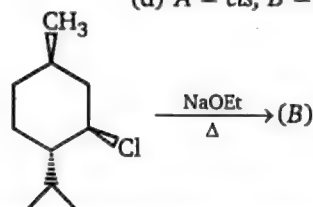
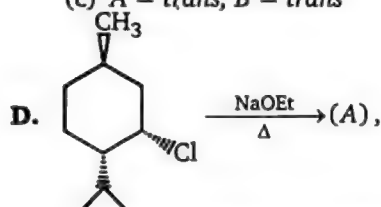
(R) (V) (VI)

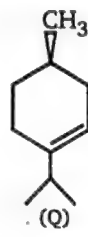
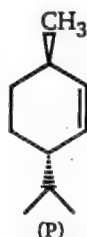
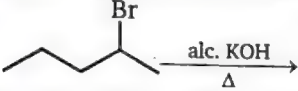
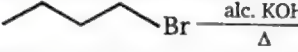
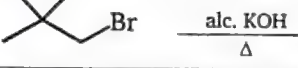
(S) Ph—CH_2—CH_2—Br (VII) Ph — CH(Br) — CH_3 (VIII)

(a) P – II, Q – III, R – VI, S – VII
(b) P – II, Q – III, R – VI, S – VI
(c) P – I, Q – III, R – VI, S – VII
(d) P – I, Q – II, R – V, S – VIII

C.

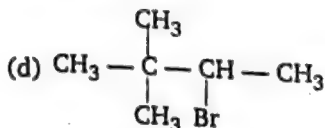
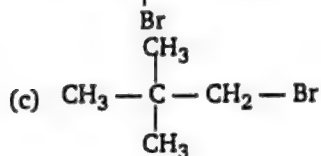
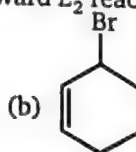
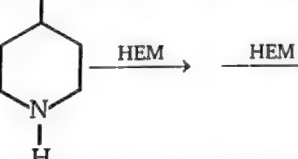
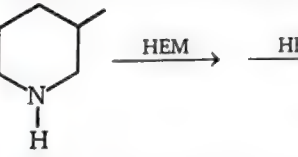
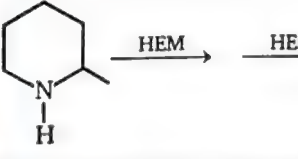
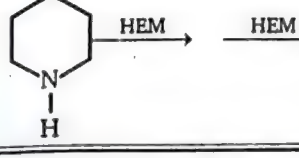
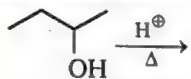
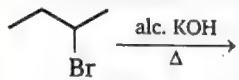
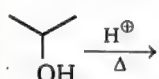
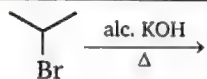
$\xrightarrow{\text{alc.KOH}}$ (B)

Product (A) and (B) are :

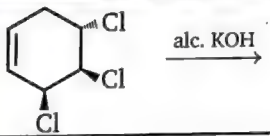
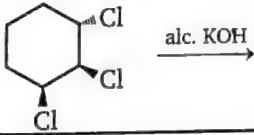
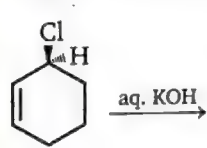
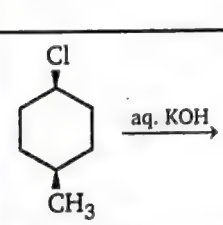
(a) A = *cis*, B = *cis*
(b) A = *trans*, B = *cis*
(c) A = *trans*, B = *trans*
(d) A = *cis*, B = *trans*

D. $\xrightarrow[\Delta]{\text{NaOEt}}$ (A), $\xrightarrow[\Delta]{\text{NaOEt}}$ (B)

Select the products (A) and (B) from the compounds (P) and (Q) given below:

(P) (Q)

(a) A = P, B = P (b) A = Q, B = Q (c) A = Q, B = P (d) A = P, B = Q

E. Which of the following compound is inert toward E_2 reaction.

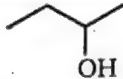
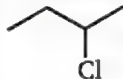
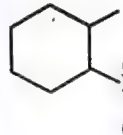
(a) $CH_3-CH(Br)-CH_2-CH_3$
(b) [bromocyclohexene structure]
(c) $CH_3-C(CH_3)_2-CH_2-Br$
(d) $CH_3-C(CH_3)_2-CH(Br)-CH_3$

2. Match the column :

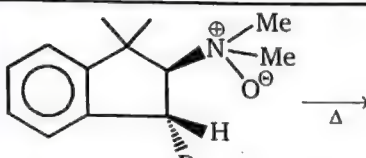
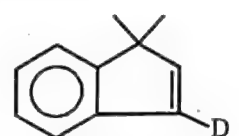
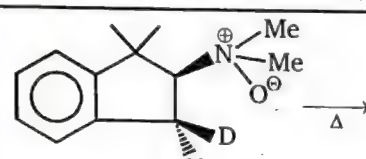
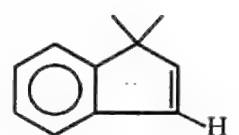
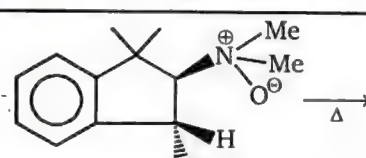
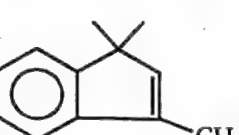
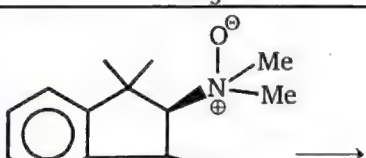
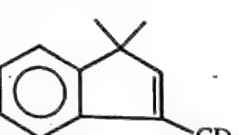
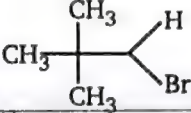
	Column (I)		Column (II)
	E_2 reaction (elimination bimolecular)		No. of possible products. (including stereoisomerism)
(a)	Br; $\xrightarrow[\Delta]{\text{alc. KOH}}$	(p)	0
(b)	Br; $\xrightarrow[\Delta]{\text{alc. KOH}}$	(q)	1
(c)	Br $\xrightarrow[\Delta]{\text{alc. KOH}}$	(r)	2
(d)	Br $\xrightarrow[\Delta]{\text{alc. KOH}}$	(s)	3

3. Match the Column :

HEM = Hoffmann exhaustive methylation followed by elimination.

	Column (I)		Column (II)
	Reaction		Product
(a)	N–H $\xrightarrow{\text{HEM}}$ $\xrightarrow{\text{HEM}}$	(p)	$H_2C=CH-CH_2-CH=CH_2$
(b)	N–H $\xrightarrow{\text{HEM}}$ $\xrightarrow{\text{HEM}}$	(q)	$H_2C=CH-CH_2-CH_2-CH=CH_2$
(c)	N–H $\xrightarrow{\text{HEM}}$ $\xrightarrow{\text{HEM}}$	(r)	$H_2C=CH-CH_2-C(CH_3)=CH_2$
(d)	N–H $\xrightarrow{\text{HEM}}$ $\xrightarrow{\text{HEM}}$	(s)	$H_2C=CH-CH(CH_3)-CH=CH_2$

4. Match the column :

	Column (I)		Column (II)
(a)	OH $\xrightarrow[\Delta]{H^{\oplus}}$	(p)	Product are Diastereomers
(b)	Br $\xrightarrow[\Delta]{\text{alc. KOH}}$	(q)	Carbocation is intermediate
(c)	OH $\xrightarrow[\Delta]{H^{\oplus}}$	(r)	2nd order reaction
(d)	Br $\xrightarrow[\Delta]{\text{alc. KOH}}$	(s)	Ist order reaction

5. Match the column :

	Column (I)		Column (II)
(a)	Cl, Cl, Cl $\xrightarrow{\text{alc. KOH}}$	(p)	Optically active product
(b)	Cl, Cl, Cl $\xrightarrow{\text{alc. KOH}}$	(q)	Optically inactive product
(c)	Cl, H $\xrightarrow{\text{aq. KOH}}$	(r)	2nd order reaction
(d)	Cl, CH_3 $\xrightarrow{\text{aq. KOH}}$	(s)	unimolecular reaction

6. **Match the column :**

	Column (I)		Column (II)
	E_2 reactions (elimination bimolecular)		Number of products (including stereoisomerism)
(a)	$CH_3-CH_2-CH_2-CH_2-Br \xrightarrow{\text{alc. KOH}}$	(p)	1
(b)	$CH_3-\underset{\underset{Br}{\vert}}{CH}-CH_2-CH_3 \xrightarrow{\text{alc. KOH}}$	(q)	2
(c)	$CH_3-\underset{\underset{Br}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_2-CH_3 \xrightarrow{\text{alc. KOH}}$	(r)	3
(d)	$Ph-CH_2-\underset{\underset{Br}{\vert}}{CH}-CH_2-CH_3$	(s)	4

7. **Match the column :**

	Column (I)		Column (II)
(a)	2-butanol (skeletal, OH) $\xrightarrow[\Delta]{H^+}$ (A)	(p)	E_1
(b)	2-chlorobutane (skeletal, Cl) $\xrightarrow[\Delta]{NaNH_2}$	(q)	E_2
(c)	$CH_3-\overset{\overset{O}{\Vert}}{C}-CH_2-\underset{\underset{Br}{\vert}}{CH}-CH_3 \xrightarrow[\Delta]{EtONa}$	(r)	Ei (elimination intramolecular)
(d)	2-methylcyclohexyl $-\overset{\oplus}{N}(Me)_2-O^{\ominus}$ $\xrightarrow{\Delta}$	(s)	E_{1CB}

8. Match the column :

Column (I)		Column (II)	
Reaction		Product	
(a)	Me, Me, $O^{\ominus}$, $\oplus$N, H, D $\xrightarrow{\Delta}$	(p)	D
(b)	Me, Me, $O^{\ominus}$, $\oplus$N, D, H $\xrightarrow{\Delta}$	(q)	H
(c)	Me, Me, $O^{\ominus}$, $\oplus$N, H, CH_3 $\xrightarrow{\Delta}$	(r)	CH_3
(d)	$O^{\ominus}$, Me, Me, N$\oplus$, D, CD_3 $\xrightarrow{\Delta}$	(s)	CD_3

9. (a) Br $\xrightarrow{\text{alc.KOH}}$ (X) products

(b) Br $\xrightarrow{\text{alc.KOH}}$ (Y)

(c) Br $\xrightarrow{\text{alc.KOH}}$ (Z)

(d) CH_3, CH_3, CH_3, H, Br $\xrightarrow{\text{alc.KOH}}$ (P)

Sum of $X + Y + Z + P =$

10. Reaction-1 : $Ph-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{PCl_5} \xrightarrow{\boxed{x}NaNH_2} \xrightarrow{CH_3I} Ph-C\equiv C-CH_3$

Reaction-2 : (2,3-dibromobutane, skeletal structure with Br, Br) $\xrightarrow{\boxed{y}NaNH_2} CH_3-C\equiv C-CH_3$

Reaction-3 : $Ph-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}} \xrightarrow{\boxed{z}NaNH_2} \xrightarrow{Et-I} Ph-C\equiv C-Et$

x, y, z are moles used.

Sum of $[\,x+y+z=\;]$

11. Sum of α-hydrogen in major product of the reaction.

Reaction-1 (cyclohexylmethanol, $C_6H_{11}-CH_2OH$) $\xrightarrow[\Delta]{H^+}$ (A)

Reaction-2 (bicyclic decalin with OH) $\xrightarrow[\Delta]{H^+}$ (B)

Reaction-3 (cyclohexyl–CH_2–CH_2–CH_2–OH) $\xrightarrow[\Delta]{H^+}$ (C)

Reaction-4 (cyclohexyl–$C(CH_3)_2$–OH) $\xrightarrow[\Delta]{H^+}$ (D)

Sum of α-hydrogen is $A+B+C+D=$

12. Reaction-1 $CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{CH_3}{\overset{|}{CH}}-CH_3 \xrightarrow[\Delta]{H^+} (A)$

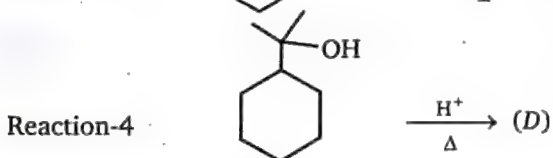
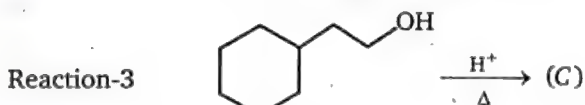
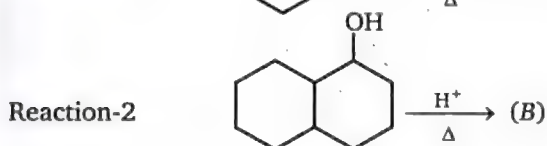
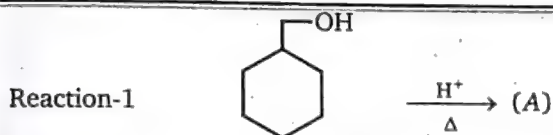
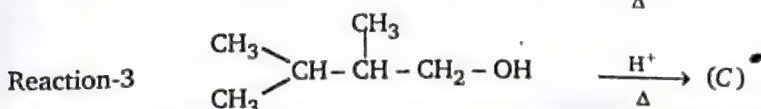
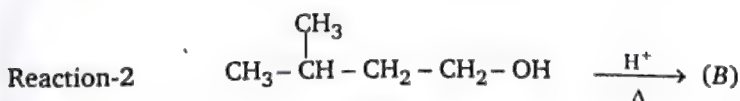
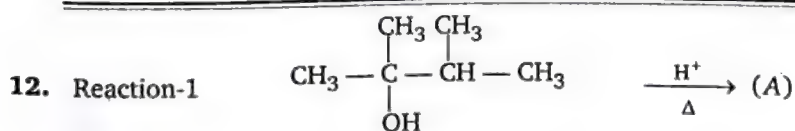
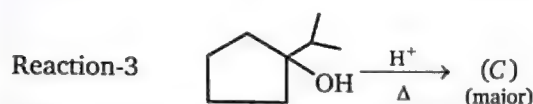
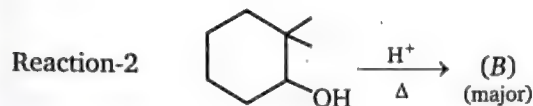
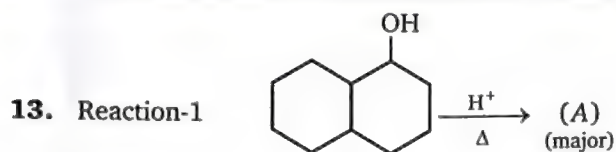
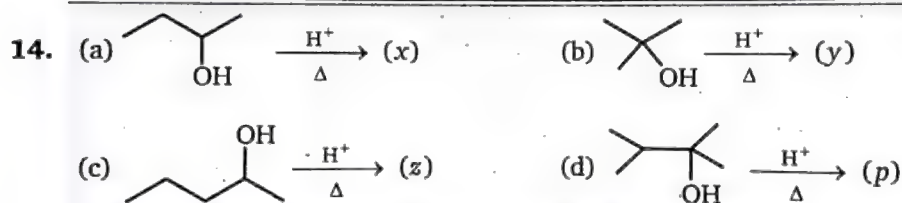
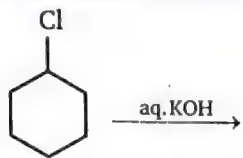
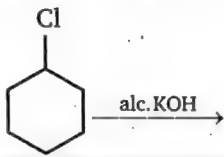
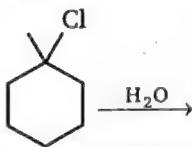
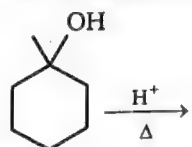
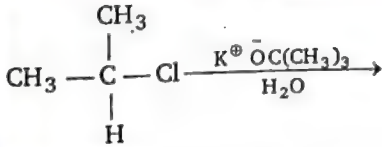
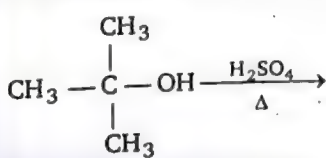
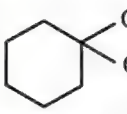
Reaction-2 $CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-OH \xrightarrow[\Delta]{H^+} (B)$

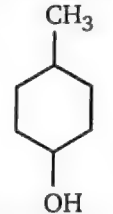
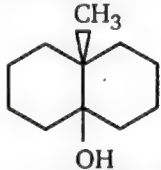
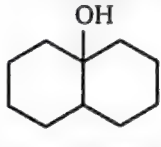
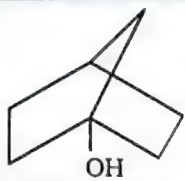
Reaction-3 $(CH_3)_2CH-\overset{CH_3}{\overset{|}{CH}}-CH_2-OH \xrightarrow[\Delta]{H^+} (C)$

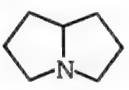
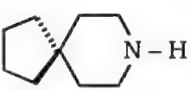
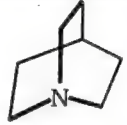
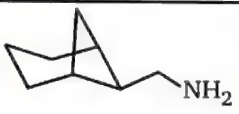
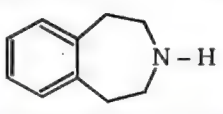
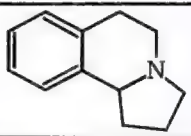
Sum of α-hydrogen is $(A+B+C=\quad)$

13. Reaction-1 (OH on decalin) $\xrightarrow[\Delta]{H^+}$ (*A*) (major)

Reaction-2 (OH) $\xrightarrow[\Delta]{H^+}$ (*B*) (major)

Reaction-3 (OH) $\xrightarrow[\Delta]{H^+}$ (*C*) (major)

Sum of α-hydrogen (*A* + *B* + *C*) =

Total number of products obtained in above reactions including minor products is (including stereoisomer)

15. Match the column (I) and (II).

	Column (I)		**Column (II)**
	Reaction		**Type of Reaction**
(a)	R -2 -chlorobutane $\xrightarrow[\text{acetone}]{\text{KSH}}$	**(p)**	S_{N^1}
(b)	R - 2- chlorobutane $\xrightarrow[\text{EtOH}]{\text{EtO}^- \overset{\oplus}{\text{Na}}}$	**(q)**	S_{N^2}
(c)	2 - bromo- 2- methyl propane $\xrightarrow{H_2O}$	**(r)**	E_1
(d)	2- butanol $\xrightarrow[\Delta]{H_2SO_4}$	**(s)**	E_2

16. Match the column (I) and (II).

	Column (I)		Column (II)
	Reaction		**Type of Reaction**
(a)	Chlorocyclohexane $\xrightarrow{\text{aq. KOH}}$	**(p)**	$S_{N}1$
(b)	Chlorocyclohexane $\xrightarrow{\text{alc. KOH}}$	**(q)**	$S_{N}2$
(c)	1-Chloro-1-methylcyclohexane $\xrightarrow{H_2O}$	**(r)**	E_1
(d)	1-Methylcyclohexanol $\xrightarrow[\Delta]{H^+}$	**(s)**	E_2

17. Select whether the following reagent combination will result in elimination or substitution reactions leading to the major product.

	Reaction	Substitution	Elimination
(a)	$CH_3-\underset{H}{\overset{CH_3}{C}}-Cl \xrightarrow[H_2O]{K^{\oplus}\ \bar{O}C(CH_3)_3}$		
(b)	$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[\Delta]{H_2SO_4}$		

(c)	$CH_3-CH(Cl)-CH_2-CH_3 \xrightarrow{\text{alc-KOH}}$		
(d)	$CH_3-C(CH_3)(H)-I \xrightarrow{\overset{\oplus}{Na}\overset{-}{N_3}}$		
(e)	1-chloro-1-methylcyclohexane (Cl, CH_3) $\xrightarrow[\Delta]{EtO^-}$		
(f)	$CH_3-C(CH_3)_2-Cl \xrightarrow{H_2O}$		

18. Match the Column (I) and (II) (Matrix).

Column (I)		Column (II)	
Reaction		Comment on product	
(a)	4-methylcyclohexanol (CH_3, OH) $\xrightarrow[\Delta]{H^+}$	(p)	Racemic mixture
(b)	decalin with CH_3 (wedge) and OH at ring junction $\xrightarrow[\Delta]{H^+}$	(q)	Major product consist of even number of α-hydrogen
(c)	decalin with OH at ring junction $\xrightarrow[\Delta]{H^+}$	(r)	Will not undergo dehydration

(d)		(s)	Major product consist of odd number of α-hydrogen

19. For each of the following amines (A through D), exhaustive methylation (treatment with excess methyl iodide), followed by Hoffmann elimination (heating with AgOH), repeated as necessary, removes the nitrogen atom in the form of trimethylamine. Indicate the number of repetitive Hoffmann eliminations required to remove the nitrogen by a number (1 to 4) in the designated answer sheet.

a.		b.		c.	
d.		e.		f.	

20.

(quinolizidine, N) ⟶ x is total number of HEM (Hoffman Exhaustive Methylation and eliminations) to remove nitrogen from given compound.

(Br) $\xrightarrow{\text{alc.KOH}}$ y is total number of possible E_2 product (including stereoisomer)

Sum of $x+y=$?

21.

$CH_3-\underset{\underset{Br}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3 \xrightarrow{\text{EtOH}}$ (x) $(S_{N^1}+E_1)$ products. (including stereoisomer)

consider all products

Total number of products are :

ANSWERS — LEVEL 2

1. A – a; B – a; C – b; D – c; E – c;
2. a – s; b – r; c – q; d – p
3. a – s; b – r; c – q; d – p
4. a – p, q, s; b – p, r; c – q, s; d – r
5. a – p, r; b – p, r; c – p, r; d – q, r
6. a – p; b – r; c – q; d – s
7. a – p; b – q; c – s; d – r
8. a – p; b – q; c – r; d – s
9. $X = 3,\ Y = 3,\ Z = 2,\ P = 0 \Rightarrow 3+3+2+0=8$
10. $x = 3,\ y = 2,\ z = 3 \Rightarrow 3+2+3=8$
11. 32
12. 33
13. 28
14. $x = 3,\ y = 1,\ z = 3,\ p = 2$

    Sum = 9
15. (a – q), (b – s), (c – p), (d – r)
16. (a – q), (b – s), (c – p), (d – r)
17. Substitution – d, f

    Elimination – a, b, c, e
18. a – p, q; b – p, q; c – q; d – r
19. a – 3; b – 2; c – 3; d – 1; e – 2; f – 3
20. 6
21. 6

5C ALKYL HALIDES

LEVEL- 1

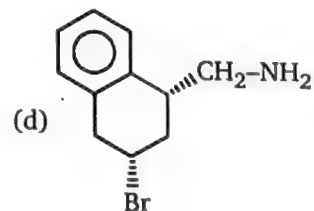
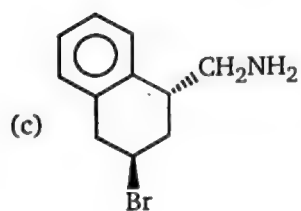
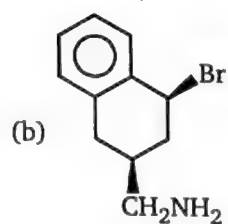
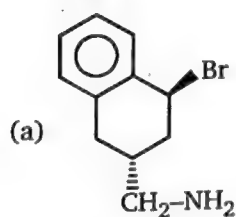
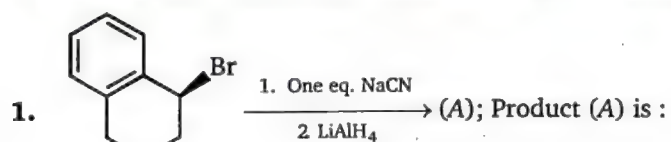
1.

$\xrightarrow[\text{2. LiAlH}_4]{\text{1. One eq. NaCN}}$ (*A*); Product (*A*) is :

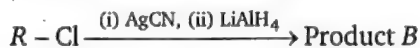
(a) Br, $CH_2–NH_2$

(b) Br, CH_2NH_2

(c) CH_2NH_2, Br

(d) $CH_2–NH_2$, Br

2. In the reactions given below,

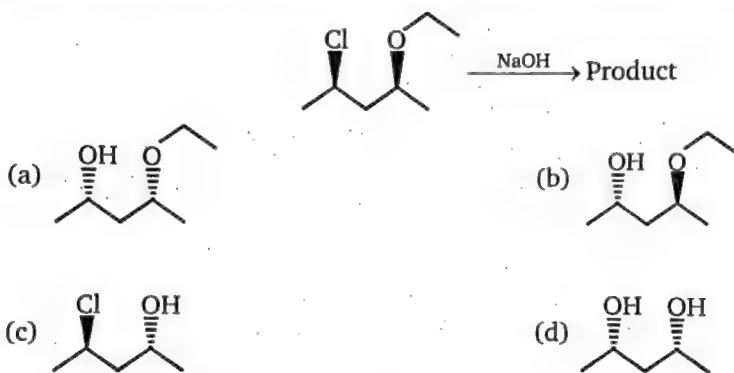
$$R - Cl \xrightarrow{\text{(i) KCN, (ii) LiAlH}_4} \text{Product } A$$

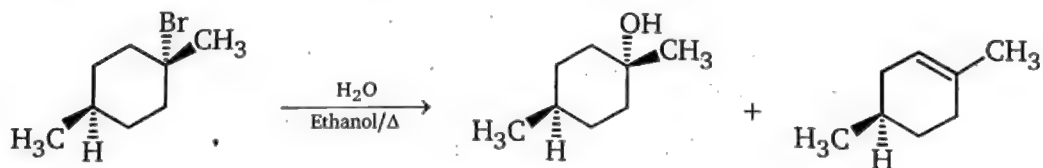
$$R - Cl \xrightarrow{\text{(i) AgCN, (ii) LiAlH}_4} \text{Product } B$$

the compounds A and B are :

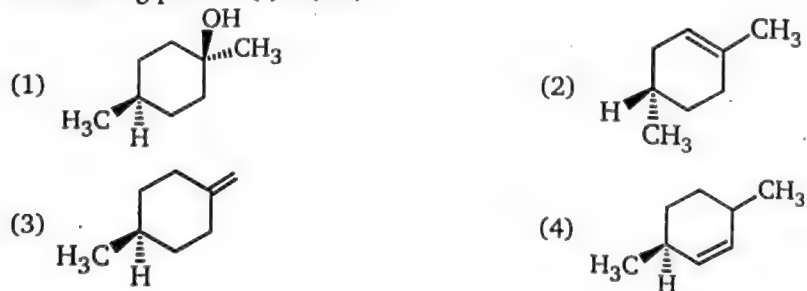
(a) chain isomers (b) position isomers
(c) functional isomers (d) metamers

3. Which is the major product expected from the following S_{N^2} reaction ?

Cl, O (ethyl) substrate $\xrightarrow{\text{NaOH}}$ Product

(a) OH O
(b) OH O
(c) Cl OH
(d) OH OH

4. Consider the following E_1/S_{N^1} reaction :

Br, CH_3, H_3C, H $\xrightarrow[\text{Ethanol}/\Delta]{H_2O}$ OH, CH_3, H_3C, H + CH_3, H_3C, H

The missing product(s) is(are) :

(1) OH, CH_3, H_3C, H
(2) CH_3, H, CH_3
(3) H_3C, H
(4) CH_3, H_3C, H

(a) 1, 2 and 3 (b) 3 and 4 (c) 2 and 3 (d) 1, 2, 3 and 4

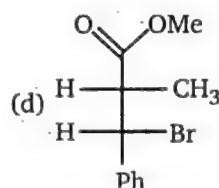
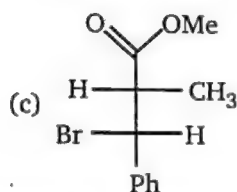
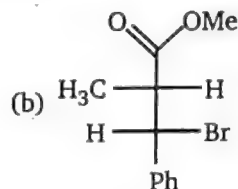
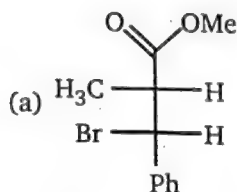
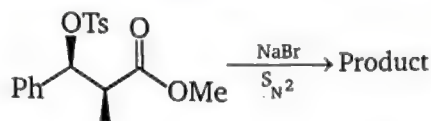
5. What is the product of the following $S_{N}2$ reaction ?

Ph–CH(OTs)–CH(CH_3)–C(=O)OMe $\xrightarrow[S_N2]{NaBr}$ Product

(a) Fischer projection: top C(=O)OMe; H_3C—C—H; Br—C—H; bottom Ph

(b) Fischer projection: top C(=O)OMe; H_3C—C—H; H—C—Br; bottom Ph

(c) Fischer projection: top C(=O)OMe; H—C—CH_3; Br—C—H; bottom Ph

(d) Fischer projection: top C(=O)OMe; H—C—CH_3; H—C—Br; bottom Ph

6. Select the reagent that will yield the greater amount of substitution on reaction with CH_3-CH_2-Br :

(a) CH_3CH_2OK in dimethyl sulfoxide (DMSO)
(b) $(CH_3)_3COK$ in dimethyl sulfoxide (DMSO)
(c) Both (a) and (b) will give comparable amounts of substitution
(d) Neither (a) nor (b) will give any amount of substitution

7. Under the specified conditions, substrate *X* undergoes substitution and elimination reactions to give products *A* – *D*. *A* and *B* are stereoisomers, but not enantiomers. *C* and *D* are enantiomers. *A* is not an isomer of *C*. Which of the following could be the starting material *X* ?

$$X \xrightarrow[\Delta]{H_2O} A + B + C + D$$

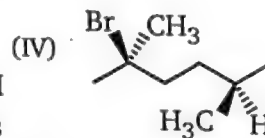
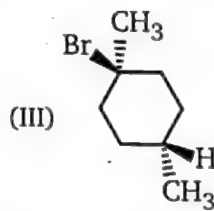
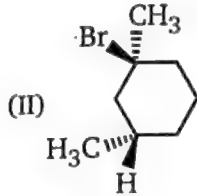
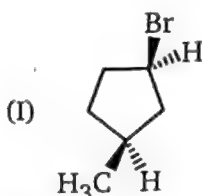
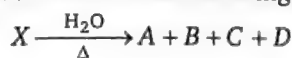
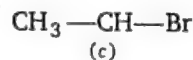
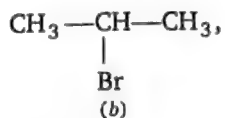
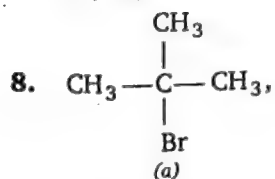
(I) cyclopentane with Br, H at one carbon and H_3C, H at another

(II) cyclohexane with Br, CH_3 at one carbon and H_3C, H at another

(III) cyclohexane with Br, CH_3 at one carbon and H, CH_3 at another

(IV) acyclic chain with Br, CH_3 at one carbon and H_3C, H at another

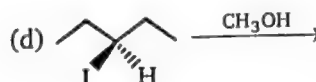
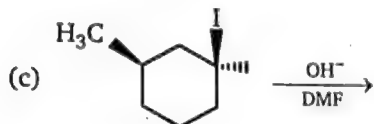
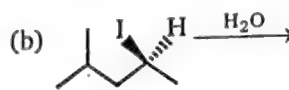
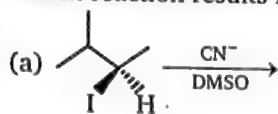
(a) (I) (b) (II) (c) (III) (d) (IV)

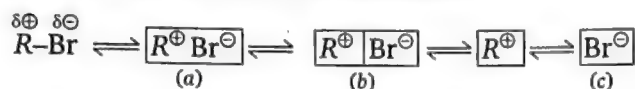
8. $CH_3-C(CH_3)(Br)-CH_3$ (a), $CH_3-CH(Br)-CH_3$ (b), CH_3-CH_2-Br (c)

Compare rate of E_2 reaction :

(a) $c > b > a$ (b) $a > b > c$ (c) $b > a > c$ (d) $c > a > b$

9. Which reaction results in the formation of a pair of enantiomers ?

(a) [structure with I and H] $\xrightarrow[DMSO]{CN^-}$ (b) [structure with I and H] $\xrightarrow{H_2O}$

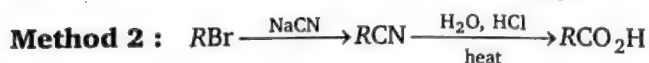
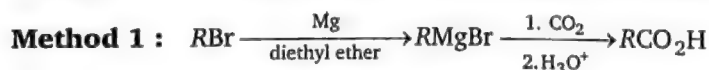
(c) [H_3C, cyclohexane with I] $\xrightarrow[DMF]{OH^-}$ (d) [structure with I and H] $\xrightarrow{CH_3OH}$

10. Rate limiting $S_{N}1$ follows the sequence

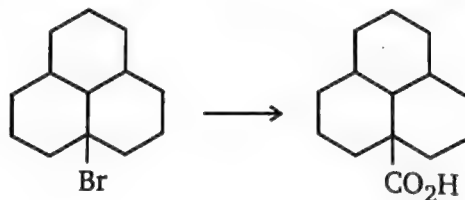
$$\overset{\delta\oplus}{R}-\overset{\delta\ominus}{Br} \rightleftharpoons \underset{(a)}{\boxed{R^{\oplus} Br^{\ominus}}} \rightleftharpoons \underset{(b)}{\boxed{R^{\oplus}}\boxed{Br^{\ominus}}} \rightleftharpoons \boxed{R^{\oplus}} \rightleftharpoons \underset{(c)}{\boxed{Br^{\ominus}}}$$

True statement about sequence on the basis of assumption that *R* contains 3 different groups is :

(a) more stable carbocation, greater is in the proportion of racemization
(b) the more nucleophilic the solvent greater in the proportion of inversion
(c) In above sequence (*b*) represent separately solvated, pair of ions
(d) All of these

11. Compare the two methods shown for the preparation of carboxylic acids :

Method 1 : $RBr \xrightarrow[\text{diethyl ether}]{Mg} RMgBr \xrightarrow[2.\,H_3O^+]{1.\,CO_2} RCO_2H$

Method 2 : $RBr \xrightarrow{NaCN} RCN \xrightarrow[\text{heat}]{H_2O,\ HCl} RCO_2H$

Which one of the following statements correctly describes this conversion ?

[tricyclic structure with Br] ⟶ [tricyclic structure with CO_2H]

(a) Both method 1 and method 2 are appropriate for carrying out this conversion
(b) Neither method 1 nor method 2 is appropriate for carrying out this conversion
(c) Method 1 will work well, but method 2 is not appropriate
(d) Method 2 will work well, but method 1 is not appropriate

12. Which of the following statements is true ?

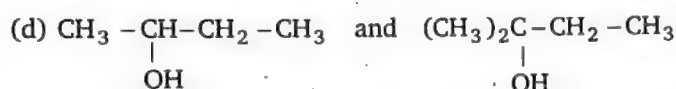
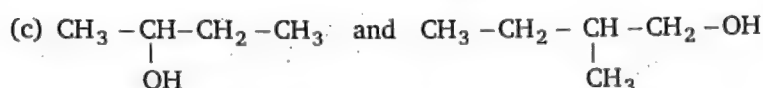
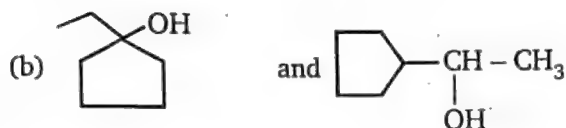
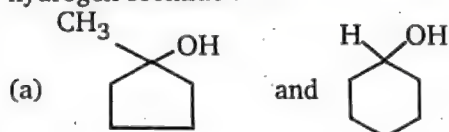
(a) $CH_3CH_2S^-$ is both a stronger base and more nucleophilic than $CH_3CH_2O^-$
(b) $CH_3CH_2S^-$ is a stronger base but is less nucleophilic than $CH_3CH_2O^-$
(c) $CH_3CH_2S^-$ is a weaker base but is more nucleophilic than $CH_3CH_2O^-$
(d) $CH_3CH_2S^-$ is both a weaker base and less nucleophilic than $CH_3CH_2O^-$

13. In the given pair of alcohols, in which pair second alcohol is more reactive than first towards hydrogen bromide ?

(a) 1-methylcyclopentanol (CH_3, OH) and cyclohexanol (H, OH)

(b) 1-ethylcyclopentanol (OH) and cyclopentyl–$\underset{OH}{CH}-CH_3$

(c) $CH_3-\underset{OH}{CH}-CH_2-CH_3$ and $CH_3-CH_2-\underset{CH_3}{CH}-CH_2-OH$

(d) $CH_3-\underset{OH}{CH}-CH_2-CH_3$ and $(CH_3)_2\underset{OH}{C}-CH_2-CH_3$

14. Which product would be expected to predominate in the given reaction ?

$C_6H_5-CH(OSO_2CF_3)-CH_2CH_3 \xrightarrow[\Delta(30°C)]{CH_3OH}$

(a) $C_6H_5-CH(OCH_3)-CH_2CH_3$

(b) $C_6H_5-CH=CH-CH_3$

(c) $C_6H_5-CH(O-SO_2-CH_3)-CH_2CH_3$

(d) None of these

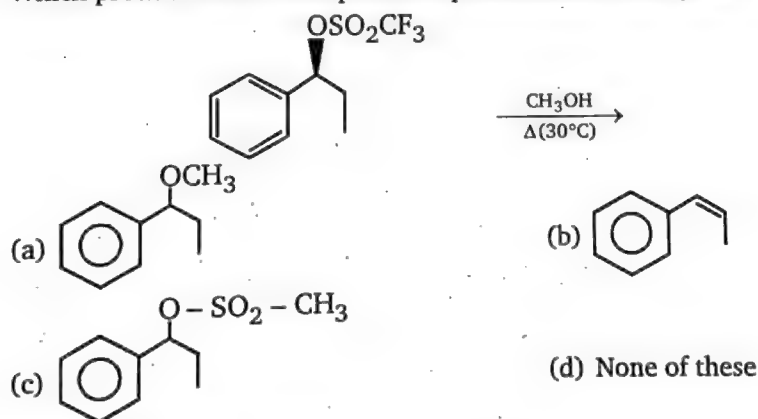
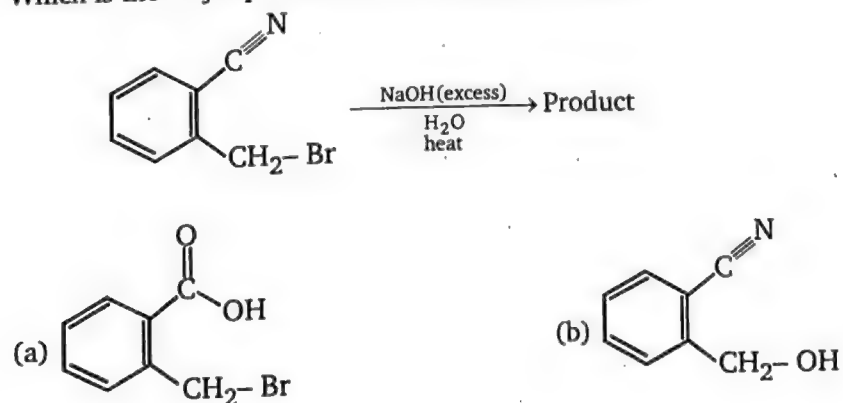
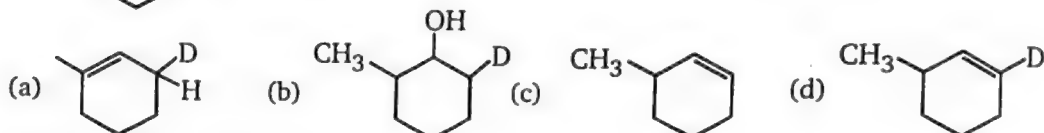
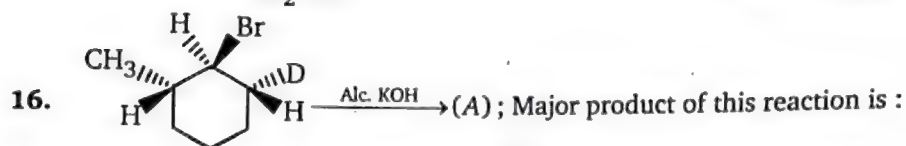
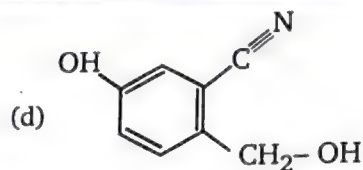
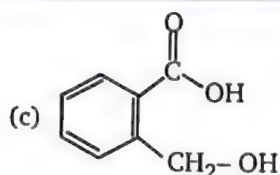
15. Which is the major product of the following reaction ?

o-($C\equiv N$)C_6H_4–CH_2-Br $\xrightarrow[H_2O,\ heat]{NaOH(excess)}$ Product

(a) o-($\overset{O}{\overset{||}{C}}-OH$)$C_6H_4$–$CH_2-Br$

(b) o-($C\equiv N$)C_6H_4–CH_2-OH

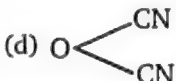
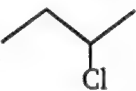
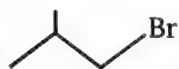
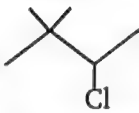
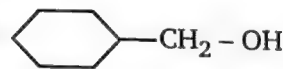
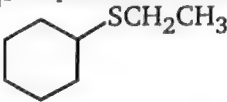
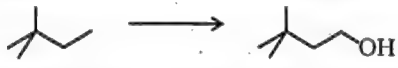
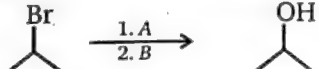
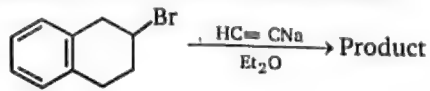
(c) (d)

16. $\xrightarrow{\text{Alc. KOH}}$ (A) ; Major product of this reaction is :

(a) (b) (c) (d)

17. Rate of S_{N^2} reaction is :

(A) (B) (C)

(a) $(B) > (A) > (C)$
(b) $(C) > (A) > (B)$
(c) $(A) > (B) > (C)$
(d) $(A) > (C) > (B)$

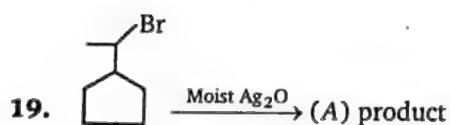
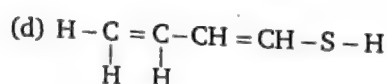
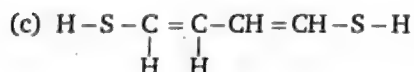
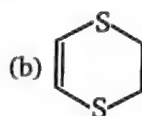
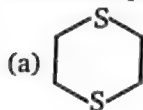
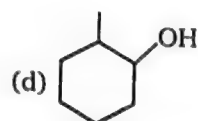
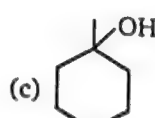
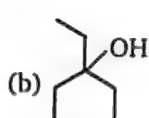
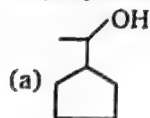
18. 1-2-dichloro ethane + $NaSCH_2CH_2SNa \longrightarrow C_4H_8S_2 + (P)$

Unknown product (P) of the above reaction is :

(a) (b)

(c) $H-S-\underset{H}{C}=\underset{H}{C}-CH=CH-S-H$

(d) $H-\underset{H}{C}=\underset{H}{C}-CH=CH-S-H$

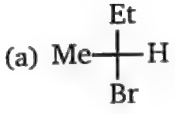
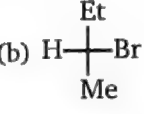
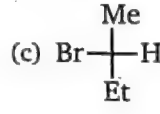
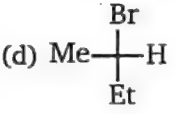
19. $\xrightarrow{\text{Moist } Ag_2O}$ (A) product

Major product (A) is :

20. MeO⌄Cl $\xrightarrow{\text{KCN}}$ Product of reaction is :

(MOM chloride)
(Methoxy methyl chloride)

(a)

(b) MeO–CH$_2$–CH$_2$... (MeO, CN)

(c) $Me-O-CH_2-CH_2-CN$

(d) $O(CN)_2$

21. In the given pair of compound, in which pair the second compound is more reactive than first toward S_{N^2} reaction ?

(a)

(b) Cyclohexyl$-CH_2-Cl$ or Cyclohexyl$-Cl$

(c) Br or Br

(d) Cl or Cl

22. Which compound might be synthesized by the S_{N^2} displacement of an alkyl-halide ?

(a) Cyclohexyl$-CH_2-OH$

(b) Cyclohexyl$-SCH_2CH_3$

(c) Me_3C-OCH_3

(d) All of these

23. Identify C in the following series $C_3H_7I \xrightarrow[\text{alc.}]{KOH} A \xrightarrow[\Delta]{NBS} B \xrightarrow[\text{alc.}]{KCN} C$.

(a) $(CH_3)_2CH-CN$

(b) $CH_2=CH-CH_2CN$

(c) $Br-CH=CH-CN$

(d) $CH_2=CH-\underset{\underset{Br}{|}}{C}HCN$

24. What sequence of reagents is required to accomplish the following transformation ?

OH

(a) (1) NBS, *ROOR* (2) $CH_3CH_2O^-$ (3) 2HBr (4) NH_2^- (5) disiamyl borane (6) H_2O_2, OH^-

(b) (1) Cl_2 hv (2) OH^-, heat; (3) 2HCl (4) OH^-, heat (5) $HgSO_4$, H_2SO_4

(c) (1) NBS, *ROOR*; OH^-, DMSO

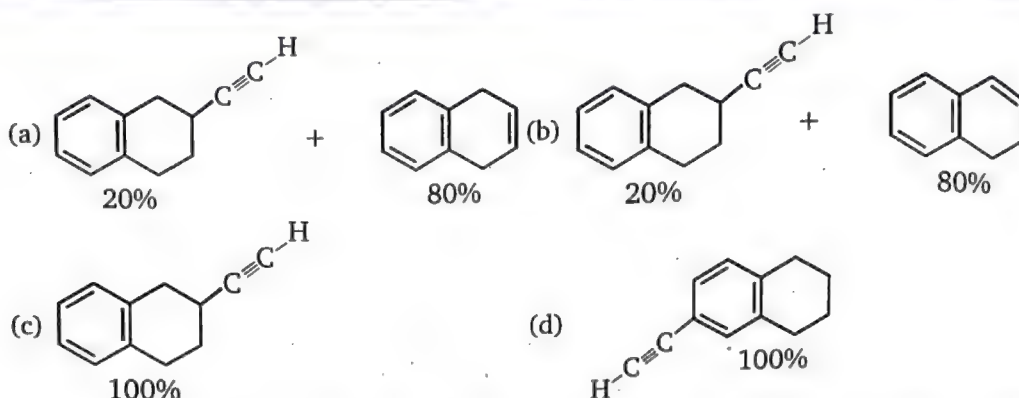
(d) (1) Br_2, hv (2) *t*-butoxide (3) BH_3, THF (4) H_2O_2, OH^-

25. Which of the reagents shown below would accomplish the following transformations?

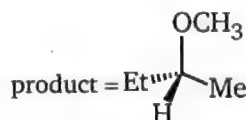
	A	*B*
(a)	H_3O^+	BH_3-THF; $H_2O_2/NaOH$
(b)	NaOH	BH_3-THF; $H_2O_2/NaOH$
(c)	HBr in ether	$Hg(OAc)_2/H_2O$; $NaBH_4$
(d)	$NaNH_2$	$Hg(OAc)_2/H_2O$; $NaBH_4$

26. What are the products obtained from the following reaction ?

Br $\xrightarrow[Et_2O]{HC\equiv CNa}$ Product

(a) [structure] 20% + [structure] 80%
(b) [structure] 20% + [structure] 80%
(c) [structure] 100%
(d) [structure] 100%

27. The back-side attack on 2-bromobutane by methoxide (CH_3O^-) gives the product shown below. Which Fischer projection represents 2-bromobutane used as the reactant in this reaction ?

product = Et–C(OCH₃)(H)–Me

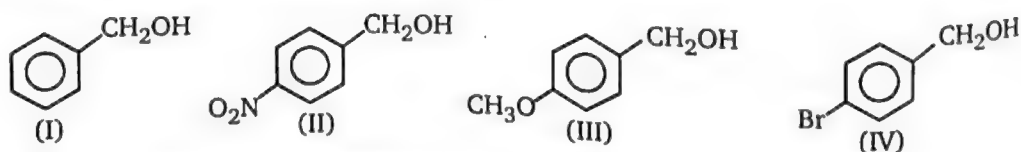
(a) Et (top), Me–|–H, Br (bottom)
(b) Et (top), H–|–Br, Me (bottom)
(c) Me (top), Br–|–H, Et (bottom)
(d) Br (top), Me–|–H, Et (bottom)

28. Consider the following statements :

(1) Bridgehead halides are inert towards both S_{N^1} and S_{N^2} reactions (till one of the ring size is eight member ring)
(2) The first step in both S_{N^1} and E_1 reactions is the same
(3) S_{N^2} reactions proceed with total retention of configuration
(4) E_2 eliminations are by the use of a solvent of low polarity and high concentration of a strong base

Which of the above statements are correct?

(a) 1, 2 and 4
(b) 1 and 3
(c) 2, 3 and 4
(d) 1, 2, 3 and 4

29. Consider the following alcohols :

(I) $C_6H_5CH_2OH$
(II) O_2N–C_6H_4–CH_2OH
(III) CH_3O–C_6H_4–CH_2OH
(IV) Br–C_6H_4–CH_2OH

The order of decreasing reactivities of these alcohols towards substitution with HBr is :

(a) III > I > IV > II
(b) III > I > II > IV
(c) I > III > IV > II
(d) I > III > II > IV

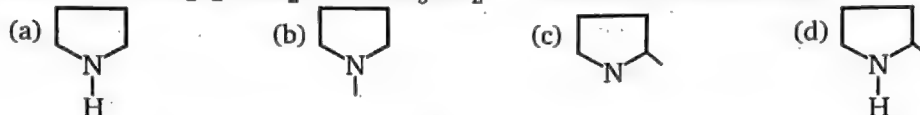
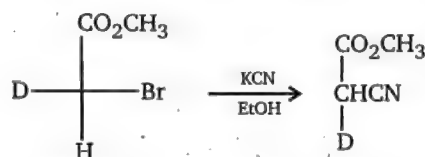
30. In solvolysis of 1,2-dimethyl propyl *p*-toluene sulfonate in acetic acid at 75°C, how many (alkene + substitution) products will be formed ?

(a) 2 (b) 3 (c) 4 (d) 5

31. Benzotrichloride reacts with milk of lime to form :

(a) Benzal (b) Benzoic acid (c) Benzyl alcohol (d) Phenol

32. $Br-CH_2-(CH_2)_2-CH_2-Br + CH_3NH_2 \longrightarrow$ Product of the reaction is :

(a)
(b)
(c)
(d)

33. The configurations of the reactant and the product in the following reaction, respectively, are:

(a) R, R (b) R, S (c) S, R (d) S, S

34. 1-4-dichlorohexane (1 mole) + NaI (1 mole) $\xrightarrow{\text{Acetone}}$ Product of the reaction is :

(a) $Cl-CH_2-CH_2-CH(I)-CH_2-CH_3$

(b) $I-CH_2-CH_2-CH(Cl)-CH_2-CH_3$

(c) $H_2C=CH-CH(Cl)-CH_2-CH_3$

(d) $I-CH_2-CH_2-CH_2-CH(Cl)-CH_2-CH_3$

35. Alkyl halides can be obtained by all methods except :

(a) $CH_3CH_2OH + HCl/ZnCl_2 \longrightarrow$

(b) $CH_3-CH_2-CH_3-CH_2 \xrightarrow{Cl_2/\text{UV light}}$

(c) $C_2H_5OH + NaCl \longrightarrow$

(d) $CH_3COOAg + Br_2/CCl_4 \longrightarrow$

36. In order to prepare 1-chloropropane, which of the following reactants can be employed ?

(a) Propene and HCl in the presence of peroxide

(b) Propene and Cl_2 followed by treatment with aq. KOH

(c) Propanol-1 and $SOCl_2$/pyridine

(d) Any of the above can be used

37. Which alkyl halide has maximum density ?

(a) C_3H_7I (b) C_2H_5I (c) CH_3I (d) CH_3Br

38. Which of the following molecules would have a carbon-halogen bond most susceptible to nucleophilic substitution ?

(a) 2-fluorobutane (b) 2-chlorobutane

(c) 2-bromobutane (d) 2-iodobutane

39. When benzyl chloride is treated with ethanolic KCN, the major product formed is :
(a) benzyl ethyl ether (b) benzyl alcohol (c) benzyl cyanide (d) benzyl isocyanide

40. Which of the following is most reactive towards nucleophilic substitution reaction ?
(a) $CH_2=CH-Cl$ (b) C_6H_5Cl
(c) $CH_3CH=CHCl$ (d) $ClCH_2-CH=CH_2$

41. Which of the following reaction will not give ether as a major product ?
(a) $CH_3CH_2Cl + Ag_2O(dry) \longrightarrow$ (b) $(CH_3)_3CCl + CH_3CH_2O^-Na^+ \longrightarrow$
(c) $CH_3CH_2Cl + Na^+O^- - C_6H_5 \longrightarrow$ (d) $CH_3Cl + Na^+O^- - C(CH_3)_2 - CH_3 \longrightarrow$

42. $O^{\ominus}-S(=O)-O^{\ominus}$ $\xrightarrow{H^+}$ (A); $\xrightarrow{CH_3-I}$ (B)

Product (A) and (B) in above reaction is :
(a) $O^- - S(=O) - O - H$, $O^- - S(=O) - O - CH_3$ (b) $O^- - S(=O) - O - H$, $O^- - {}^{\oplus}S(=O)(O^-) - CH_3$
(c) $O^- - S(=O) - O - CH_3$, $O^{\ominus} - {}^{\oplus}S(=O)(CH_3) - H$ (d) $O^- - {}^{\oplus}S(=O)(H) - O$, $O^- - S(=O)(CH_3) - O^-$

ANSWERS — LEVEL 1															
1.	(c)	**2.**	(c)	**3.**	(b)	**4.**	(a)	**5.**	(a)	**6.**	(a)	**7.**	(c)	**8.**	(b)
9.	(b)	**10.**	(d)	**11.**	(c)	**12.**	(c)	**13.**	(d)	**14.**	(a)	**15.**	(c)	**16.**	(c)
17.	(c)	**18.**	(a)	**19.**	(c)	**20.**	(b)	**21.**	(d)	**22.**	(d)	**23.**	(b)	**24.**	(d)
25.	(d)	**26.**	(b)	**27.**	(d)	**28.**	(a)	**29.**	(a)	**30.**	(d)	**31.**	(b)	**32.**	(b)
33.	(d)	**34.**	(d)	**35.**	(c)	**36.**	(c)	**37.**	(a)	**38.**	(d)	**39.**	(c)	**40.**	(d)
41.	(b)	**42.**	(b)												

LEVEL-2

1. The following organic halide derivatives (*A* to *J*) are reacted in ethanol solution with each of the nucleophiles : acetate, methylthiolate, cyanide and hydroxide anions. Six possible results from these combinations of reactants are designated (1) through (6) below :

   Write the number corresponding to your best estimate of the outcome of each reaction in the appropriate answer box below.

Cl	CH_2-Cl	CH_3-I	H_3C, H_3C, Cl, H	Cl, CH_3
A	*B*	*C*	*D*	*E*
Br	Cl	H, Br, H, H	CH_2-Br, H, H, H_3C	Br, CH_3, H, H_3C
F	*G*	*H*	*I*	*J*

Possible Outcome :

(1) No reaction
(2) Substitution
(3) Elimination
(4) Substitution and elimination
(5) No reaction or slow substitution
(6) No reaction or slow elimination

	Compound	A	B	C	D	E	F	G	H	I	J
(i)	**CH_3CO_2Na**										
(ii)	**CH_3SNa**										
(iii)	**NaCN**										
(iv)	**NaOH**										

2. In each of the following sections three organic halogen compounds are listed. In the box given enter a number (1 to 3) indicating the order of reactivity of the designated (1 is most reactive and 3 is least).

(a) S_{N^2} substitution by $NaOCOCH_3$ in methanol:
1. $CH_3CH_2CH_2Br$ ☐ 2. $(CH_3)_2CHBr$ ☐ 3. $CH_2=CHCH_2Br$ ☐

(b) S_{N^2} substitution by NaI in acetone:
1. C_6H_5Cl ☐ 2. $C_6H_5CH_2Cl$ ☐ 3. $C_6H_5CHClCH_3$ ☐

(c) S_{N^2} substitution by NaCN in methanol:
1. CH_3CH_2Cl ☐ 2. CH_3CH_2F ☐ 3. CH_3CH_2I ☐

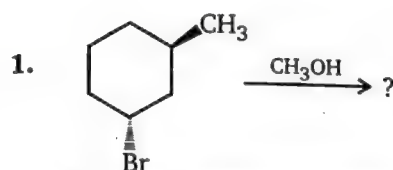
(d) S_{N^2} substitution by $NaSCH_3$ in methanol:
1. $(CH_3)_2CHCH_2CH_2Br$ ☐ 2. $CH_3CH_2CHBrCH_2CH_3$ ☐ 3. $(CH_3)_3CCH_2Br$ ☐

3. Isobutyl alcohol (2-methyl-1-propanol), $(CH_3)_2CHCH_2OH$, can be transformed to each of the compounds (a through l) listed in the left-hand column. In each case the number of steps needed to accomplish the change is noted, and an answer box is provided for your reagent selections. Fourteen reagents (designated A through N) are listed in the right-hand column.

Write letters designating the reagent or reagents you believe will achieve the desired transformation in the box to the right of the product formula. In the case of a multi-step sequence write the reagents in the order they are to be used. In some cases you may wish to use a previously prepared compound as a reactant. If so, write the number (a to l) corresponding to the desired compound.

	Desired product	No. of Steps	Write Options		Reagent List
a.	$(CH_3)_2CHCH_2Br$	one		**A.**	$Hg(OAc)_2$ in H_2O
b.	$(CH_3)_2C=CH_2$	one		**B.**	PBr_3 & heat
c.	$(CH_3)_2CHCH=O$	one		**C.**	$NaBH_4$ in alcohol
d.	$(CH_3)_2CHCO_2H$	one		**D.**	$LiAlH_4$ in THF (aqueous workup)
e.	$(CH_3)_3CBr$	two		**E.**	NaCN in alcohol
f.	$(CH_3)_2CHCH_2C\equiv N$	two		**F.**	PCC in CH_2Cl_2
g.	$(CH_3)_2CHCH_2OCOCH_3$	one		**G.**	Jones' reagent (CrO_3 in H_3O^+)
h.	$(CH_3)_2CHCO_2C_2H_5$	two		**H.**	HBr in CH_2Cl_2
i.	$(CH_3)_2CHCH_2OCH_2(CH_3)$	two		**I.**	H_3PO_4 and heat
j.	$(CH_3)_3COH$	three		**J.**	$(CH_3CO)_2O$ + pyridine
k.	$(CH_3)_2CHCH_2NH_2$	three		**K.**	NaN_3 in aqueous alcohol
l.	$(CH_3)_2CHCH_2CH_2NH_2$	two		**L.**	$C_6H_5CO_3H$ in CH_2Cl_2 (peracid)
				M.	NaH in ether and heat
				N.	C_2H_5OH + acid catalyst & heat

SUBJECTIVE PROBLEMS

1. (3-methylcyclohexyl bromide: ring with wedged CH_3 and wedged Br) $\xrightarrow{CH_3OH}$?

X = Total number of substitution and elimination product(s). Find the value of X.

ANSWERS — LEVEL 2

1.

	A	B	C	D	E	F	G	H	I	J
(i)	2	2	2	1	1	1	6	2	2	6
(ii)	2	2	2	1	1	5	6	2	2	6
(iii)	2	2	2	1	1	1	3	3	2	3
(iv)	4	2	2	1	1	5	3	3	4	3

2. a – 3 > 1 > 2; b – 2 > 3 > 1; c – 3 > 1 > 2; d – 1 > 2 > 3

3. a – B; b – I; c – F; d – G; e – I, H or 2 H; f – B, E or 1, E; g – J; h – G, N or 4N
i – N, j – I, A, C or 2AC or ILD or 2LD; k – B, K, D or 1KD; l – B, E, D or 1ED or 6D

Subjective Problems

1. 4

6 ALCOHOL, ETHERS AND EPOXIDES

LEVEL- 1

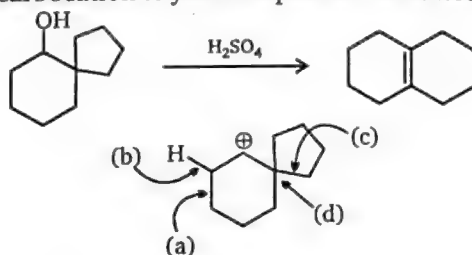
1. The following transformation involves a carbocation rearrangement. The carbocation is generated by protonation of the hydroxyl group, followed by the loss of water. Which bond has to migrate in the carbocation to yield the product indicated (after the deprotonation) ?

OH

$\xrightarrow{H_2SO_4}$

(b) H ⊕ (c)

(d)

(a)

(a) a (b) b (c) c (d) d

2. Identify the major product.

HO

$\xrightarrow{H_2SO_4}$ Product

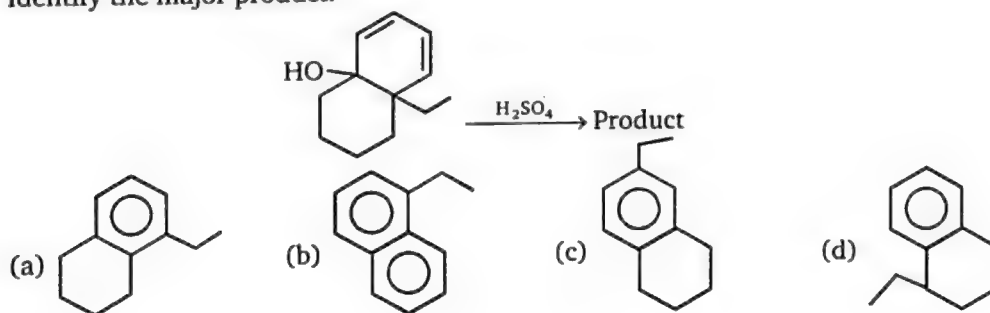
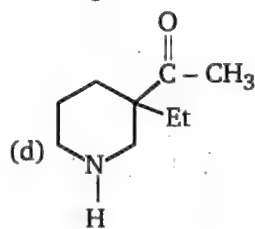
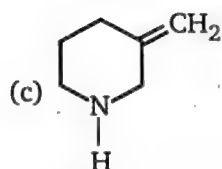
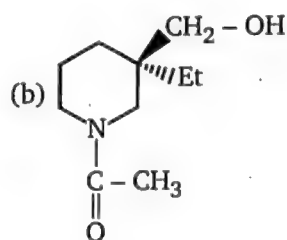
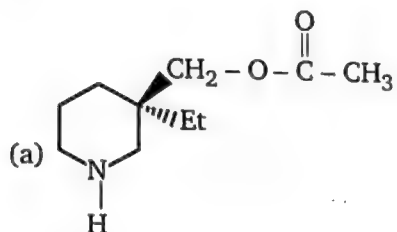
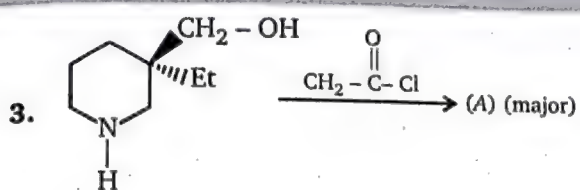
(a) (b) (c) (d)

3. (Piperidine ring with N–H; ring carbon bearing CH_2-OH (wedge) and Et (hash)) $\xrightarrow{CH_2-\overset{O}{\overset{||}{C}}-Cl}$ (A) (major)

(a) (Piperidine N–H; ring carbon bearing $CH_2-O-\overset{O}{\overset{||}{C}}-CH_3$ and Et)

(b) (Piperidine with N–$\underset{O}{\underset{||}{C}}-CH_3$; ring carbon bearing CH_2-OH and Et)

(c) (Piperidine N–H with exocyclic $=CH_2$)

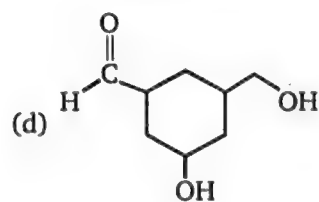
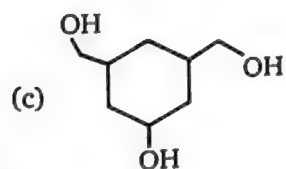
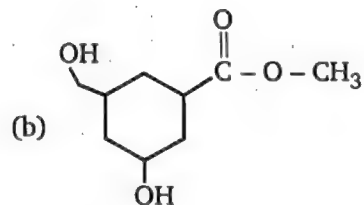
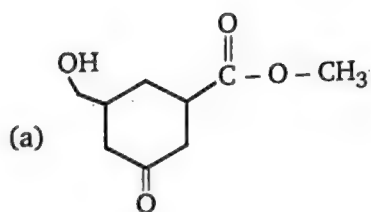
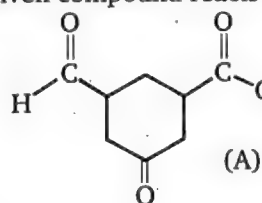
(d) (Piperidine N–H; ring carbon bearing $\overset{O}{\overset{||}{C}}-CH_3$ and Et)

4. Predict the product when given compound reacts with $LiAlH_4$:

(A): cyclohexanone ring bearing $H-\overset{O}{\overset{||}{C}}-$ and $-\overset{O}{\overset{||}{C}}-OCH_3$ groups

(a) Ring with CH_2OH, $-\overset{O}{\overset{||}{C}}-O-CH_3$ and ring $C=O$

(b) Ring with CH_2OH, $-\overset{O}{\overset{||}{C}}-O-CH_3$ and ring OH

(c) Ring with CH_2OH, CH_2OH and ring OH

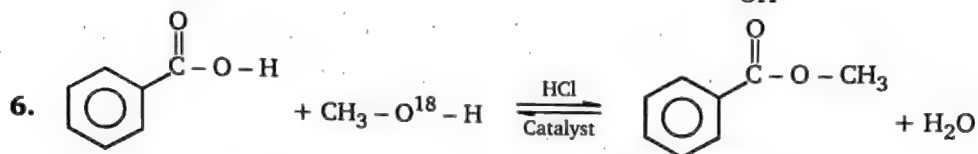
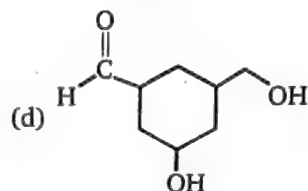
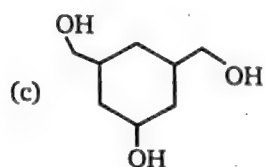
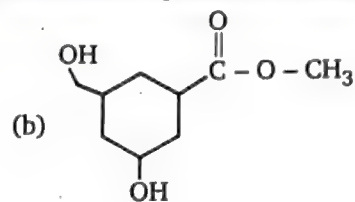
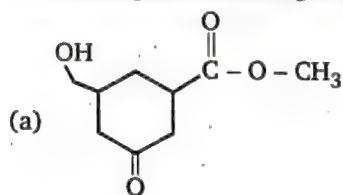
(d) Ring with $H-\overset{O}{\overset{||}{C}}-$, CH_2OH and ring OH

5. Predict the product when given compound (*A*, in the above question 4) reacts with $NaBH_4$.

(a) OH, $-\overset{O}{\overset{\|}{C}}-O-CH_3$, =O

(b) OH, $-\overset{O}{\overset{\|}{C}}-O-CH_3$, OH

(c) OH, OH, OH

(d) $H-\overset{O}{\overset{\|}{C}}-$, OH, OH

6. $C_6H_5-\overset{O}{\overset{\|}{C}}-O-H + CH_3-O^{18}-H \underset{\text{Catalyst}}{\overset{\text{HCl}}{\rightleftharpoons}} C_6H_5-\overset{O}{\overset{\|}{C}}-O-CH_3 + H_2O$

Methyl benzoate

The labelled $-O^{18}$ will be in :

(a) H_2O

(b) Methyl benzoate

(c) Both (a) and (b)

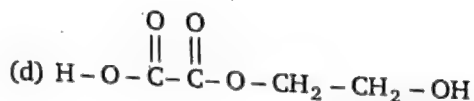
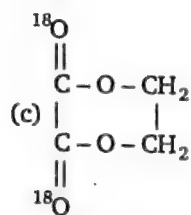
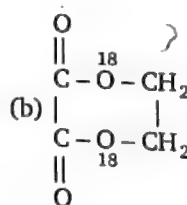
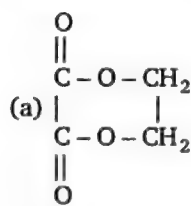
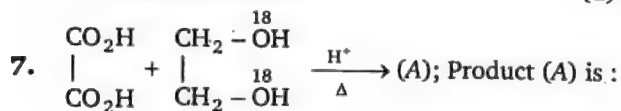
(d) Benzoic acid

7. $\begin{array}{l} CO_2H \\ | \\ CO_2H \end{array} + \begin{array}{l} CH_2-\overset{18}{O}H \\ | \\ CH_2-\overset{18}{O}H \end{array} \xrightarrow[\Delta]{H^+} (A)$; Product (*A*) is :

(a) $\begin{array}{l} \overset{O}{\overset{\|}{C}}-O-CH_2 \\ | \qquad\quad | \\ \underset{\|}{C}-O-CH_2 \\ O \end{array}$

(b) $\begin{array}{l} \overset{O}{\overset{\|}{C}}-\overset{18}{O}-CH_2 \\ | \qquad\quad | \\ \underset{\|}{C}-\underset{18}{O}-CH_2 \\ O \end{array}$

(c) $\begin{array}{l} \overset{^{18}O}{\overset{\|}{C}}-O-CH_2 \\ | \qquad\quad | \\ \underset{\|}{C}-O-CH_2 \\ ^{18}O \end{array}$

(d) $H-O-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-OH$

8. Which is oxidized most easily ?

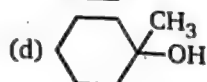
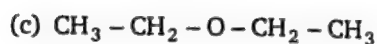
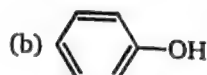
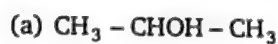
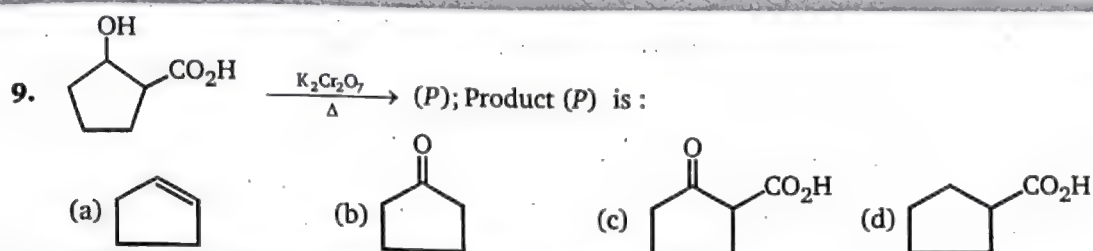
(a) $CH_3-CHOH-CH_3$

(b) C_6H_5-OH

(c) $CH_3-CH_2-O-CH_2-CH_3$

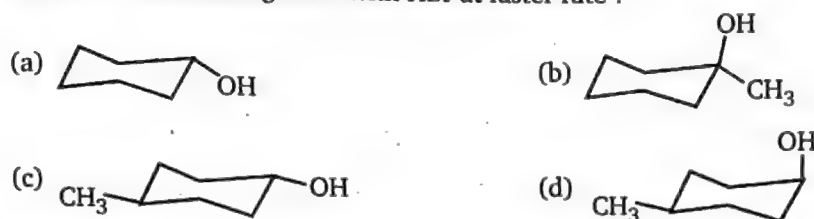
(d) 1-methylcyclohexanol (CH_3, $-OH$)

9. (2-hydroxycyclopentanecarboxylic acid: cyclopentane with OH and CO_2H) $\xrightarrow[\Delta]{K_2Cr_2O_7}$ (P); Product (P) is :

(a) cyclopentene (b) cyclopentanone (c) 2-oxocyclopentanecarboxylic acid (CO_2H) (d) cyclopentanecarboxylic acid (CO_2H)

10. Which of the following react with HBr at faster rate ?

(a) cyclohexane with OH (b) cyclohexane with OH and CH_3

(c) CH_3–cyclohexane–OH (d) CH_3–cyclohexane with axial OH

11. $CH_3-\overset{O}{\overset{||}{C}}-C_6H_{10}-\overset{O}{\overset{||}{C}}-OH \longrightarrow CH_3-\overset{OH}{\overset{|}{CH}}-C_6H_{10}-CH_2-OH$

Above conversion can be done by :

(a) $NaBH_4$ (b) $LiAlH_4$ (c) PCC (d) $KMnO_4$

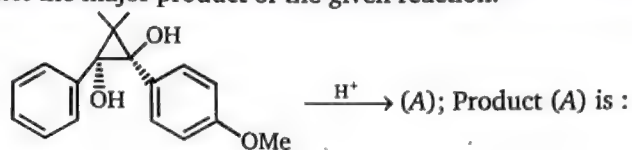
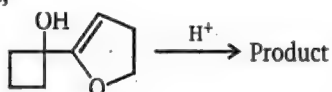
12. $HO_2C-C_6H_4-CO_2H$ (para) $\xrightarrow[H_2SO_4, \Delta]{2\ CH_3OH}$ (A) ; Product (A) is :

(a) $CH_3O_2C-C_6H_4-CO_2H$ (para) (b) $CH_3O_2C-C_6H_4-CO_2CH_3$ (para) (c) $CH_3O_2C-C_6H_4-CO_2CH_3$ (meta) (d) $CH_3-\overset{O}{\overset{||}{C}}-C_6H_4-\overset{O}{\overset{||}{C}}-CH_3$ (para)

13. (1-hydroxycyclopentyl, C1–C5, bonded to C6 bearing OH, Ph, Ph) $\xrightarrow[99\%\text{yield}]{H_2SO_4}$ (P) ; Unknown (P) of the reaction is :

(a) cyclohexanone (C1 = C=O; C6 bearing Ph, Ph; ring atoms 1–6) (b) cyclopentylidene (C1=C6) with C6 bearing Ph, Ph

(c) cyclohexanone (C6 = C=O; C1 bearing Ph, Ph; ring atoms 1–6) (d) cyclopentyl (C1) attached to C6 bearing OH, Ph, Ph

14. Predict the major product of the given reaction.

OH, OH, OMe $\xrightarrow{H^+}$ (*A*); Product (*A*) is :

(a) OMe (b) OMe

(c) MeO, O (d) O, OMe

15. Identify the major product,

OH, O $\xrightarrow{H^+}$ Product

(a) O, O (b) OH, O (c) O, O (d) O, O

16. O, O $\xrightarrow{H^+}$ (*A*); Product (*A*) is :

(a) O, O (b) O, O (c) O, O (d) O, O

17. OCH_3, OCH_3, CO_2CH_3 $\xrightarrow{LiAlH_4}$ (*A*) Major; product (*A*) is :

(a) OH, OCH_3, CH_2OH (b) O, OH (c) OH, OH (d) OCH_3, OCH_3, CH_2OH

18. (Resorcinol) $\xrightarrow{I_2+NaOH}$ CHI_3 (Iodoform) + (A); Compound (A) is :

(a) $CH_2(CO_2Na)-CH=CH-COO^{\ominus}Na^{\oplus}$

(b) $H-O-\overset{O}{\overset{||}{C}}-(CH_2)_2-\overset{O}{\overset{||}{C}}-OH$

(c) $CH_3-CH_2-CH_2-CH_2-\overset{O}{\overset{||}{C}}-OH$

(d) $CH_3-(CH_2)_3-\overset{O}{\overset{||}{C}}-ONa$

19. (3° alcohol) $\xrightarrow{H_2CrO_4}$ (A). Product (A) is :

(a) No reaction (b) (c) (d) OH

20. CO_2H $\xrightarrow[(2)\ H^{\oplus}]{(1) CH_3-Li(excess)}$ (A) $\xrightarrow[NaOH]{I_2}$ (B) + $CHI_3\downarrow$; Compound (B) is :

(a) $\overset{O}{\overset{||}{C}}-\overset{-}{O}\overset{+}{Na}$ (b) $\overset{O}{\overset{||}{C}}-\overset{-}{O}\overset{+}{Na}$ (c) CO_2Na (d) CO_2Na

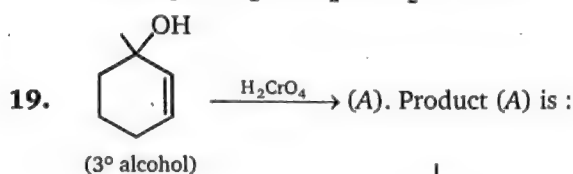
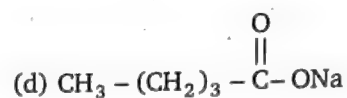
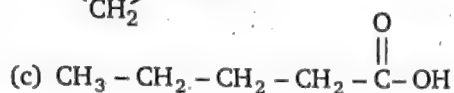
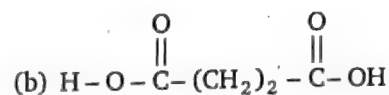
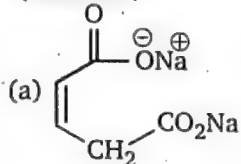
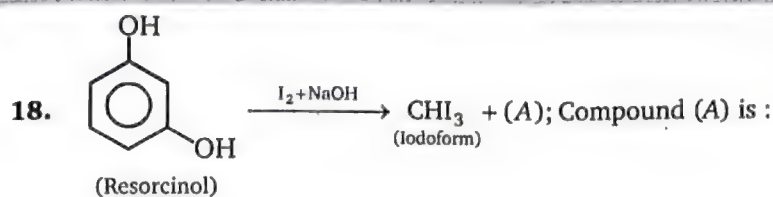
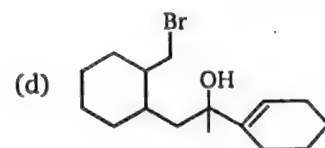
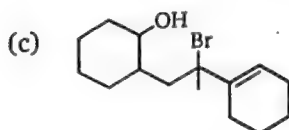
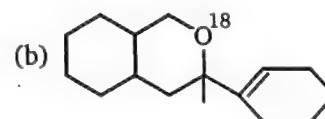
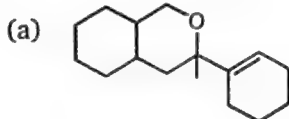
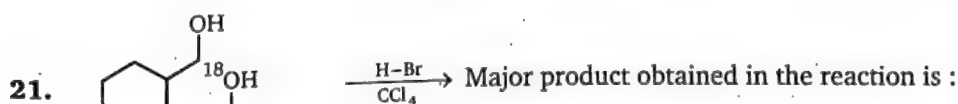
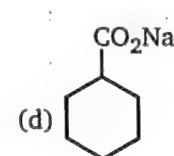
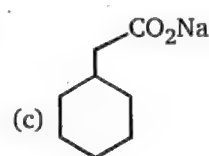
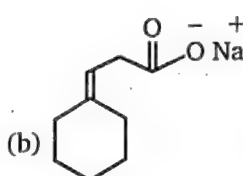
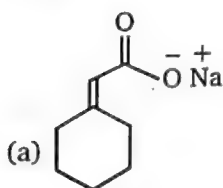
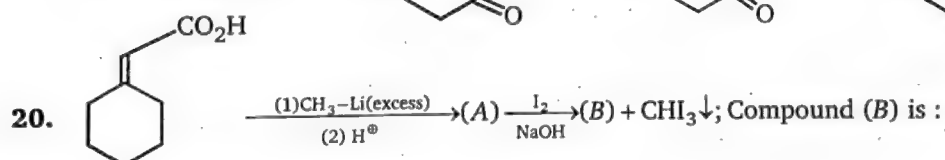
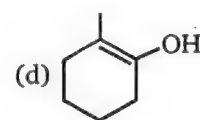
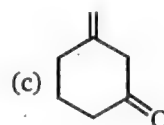
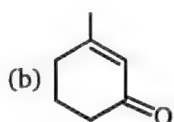
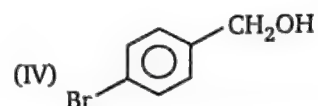
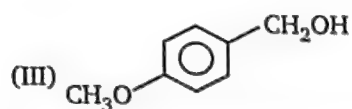
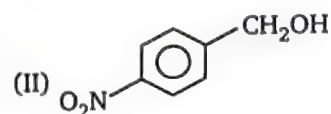
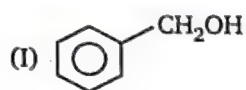
21. OH, ^{18}OH $\xrightarrow[CCl_4]{H-Br}$ Major product obtained in the reaction is :

(a) O (b) O^{18}

(c) OH, Br (d) Br, OH

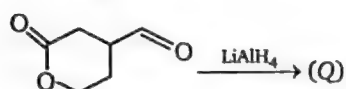
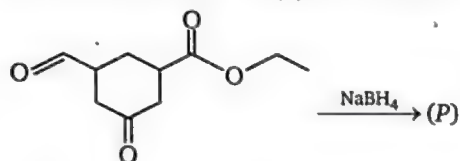
22. Consider the following alcohols,

(I) $C_6H_5CH_2OH$ (II) $O_2N-C_6H_4-CH_2OH$

(III) $CH_3O-C_6H_4-CH_2OH$ (IV) $Br-C_6H_4-CH_2OH$

The order of decreasing reactivities of these alcohols towards nucleophilic substitution with HBr is:

(a) III > I > IV > II (b) III > I > II > IV (c) I > III > IV > II (d) I > III > II > IV

23. $\xrightarrow{NaBH_4} (P)$

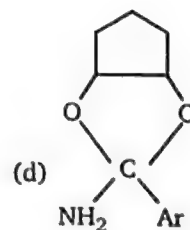
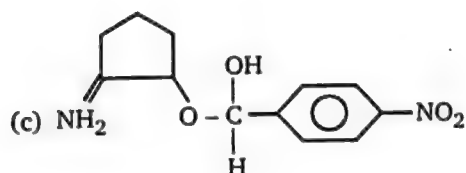
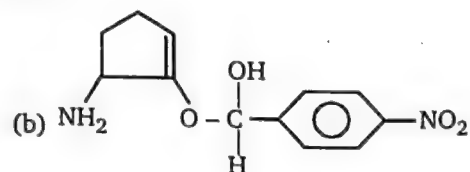
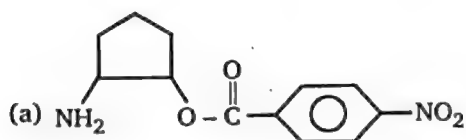
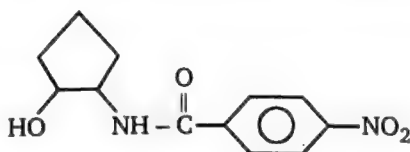
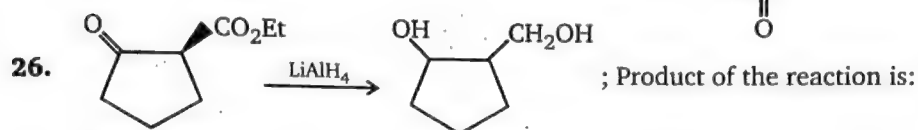
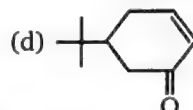
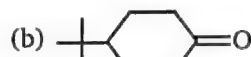
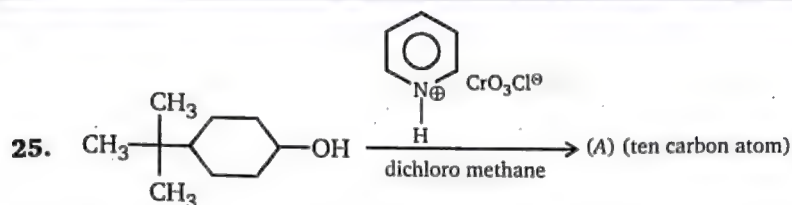
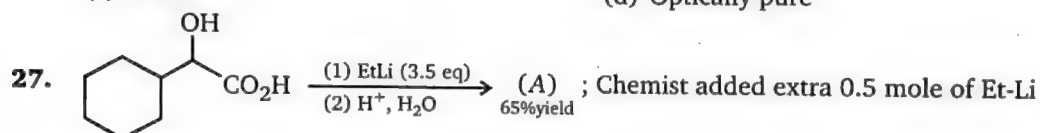
$\xrightarrow{LiAlH_4} (Q)$

Sum of number of 1° alcoholic groups in product (*P*) and (*Q*) is:

(a) 1 (b) 2 (c) 3 (d) 5

24. In presence of dil. HCl, compound *A* is converted to a constitutional isomer (*B*), compound *B* is:

HO NH – C(=O) – C_6H_4 – NO_2

(a) NH_2 O – C(=O) – C_6H_4 – NO_2 (b) NH_2 O – C(OH)(H) – C_6H_4 – NO_2

(c) NH_2 O – C(OH)(H) – C_6H_4 – NO_2 (d) O O C NH_2 Ar

25.
CH3
CH3
CH3
OH
N⊕ CrO3Cl⊖
H
dichloro methane
(A) (ten carbon atom)
(a)
(b)
O
(c)
(d)
O
26.
O
CO2Et
LiAlH4
OH
CH2OH
; Product of the reaction is:
(a) Racemic
(b) Diastereomer
(c) Meso
(d) Optically pure
27.
OH
CO2H
(1) EtLi (3.5 eq)
(2) H+, H2O
(A)
65%yield
; Chemist added extra 0.5 mole of Et-Li
in above reaction to obtain product (A), which is?
(a)
O O
Et
(b)
OH
O
C – Et
(c)
O
Et
(d)
O
Et
28.
CH2OH
O
HO
+ Ph – C – O – H
HCl
Major product of above esterification reaction is:
(a)
O
OH
Ph
O
(b)
O
CH2 – O – C – Ph
HO
(c)
CH2 – O – Ph
HO
(d)
O
O – C – Ph
HO

29. ^{14}C label → ; no label → OTs $\xrightarrow{RCO_2H}$; OCOR + OCOR

(a) S_{N^1} (b) S_{N^2} (c) SN — NGP (d) SN — Ar

30. HO–C_6H_4–NH_2 $\xrightarrow[100°C]{AC_2O}$ (A); Product (A) of reaction is :

(a) O–C(=O)– / NH–C(=O)– (b) O–C(=O)– / NH_2 (c) OH / NH–C(=O)– (d) O–C(=O)– / NH–C(=O)–

31. OH / $CH_3-\overset{|}{C}-OH$ / CH_3 $\xrightarrow{\text{(pyridinium, } \oplus N-H\text{) } CrO_3Cl^{\ominus}\text{, (PCC).}CH_2Cl_2}$ Product of the reaction is :

(a)

(b) CHO, OH (c) CO_2H, OH (d) O, OH

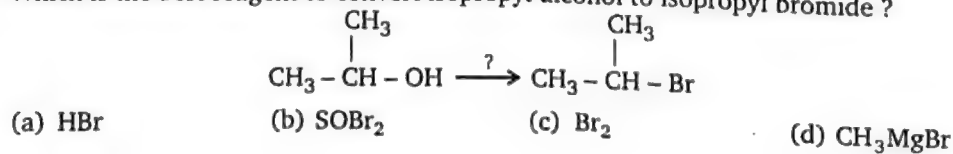
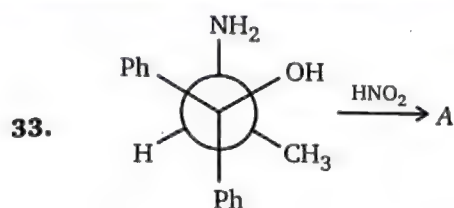
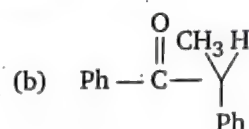
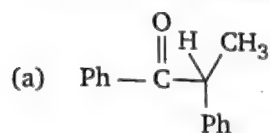
32. Which is the best reagent to convert isopropyl alcohol to isopropyl bromide ?

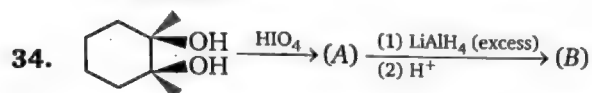
$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{CH}}}-OH \xrightarrow{?} CH_3-\overset{CH_3}{\overset{|}{CH}}-Br$$

(a) HBr (b) $SOBr_2$ (c) Br_2 (d) CH_3MgBr

33. (Newman projection: front — NH_2, OH, Ph; back — Ph, H, CH_3) $\xrightarrow{HNO_2}$ *A*

Major product obtained in the above reaction is :

(a) $Ph-\overset{O}{\overset{\|}{C}}-C(H)(CH_3)(Ph)$ (b) $Ph-\overset{O}{\overset{\|}{C}}-C(CH_3)(H)(Ph)$

(c) Racemic (d) Diastereomers

34. (cyclohexane-1,2-diol) $\xrightarrow{HIO_4}$ (A) $\xrightarrow[(2)\ H^+]{(1)\ LiAlH_4\ (excess)}$ (B)

Total number of stereoisomers of product (B) will be:

(a) 2 (b) 3 (c) 4 (d) 5

35. (cyclopentane with $S-\overset{O}{\overset{\|}{C}}-CH_3$ and $O-\underset{O}{\underset{\|}{C}}-CH_3$) $\xrightarrow[2.\ H^+]{1.\ HO^-}$ Major product of the reaction is :

(c)

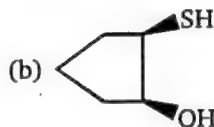
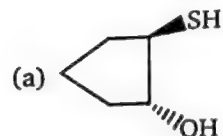
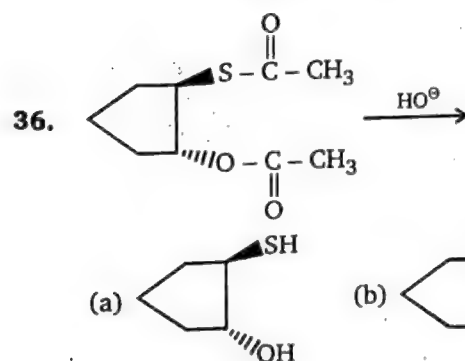
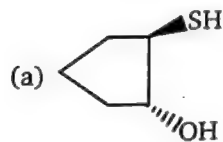
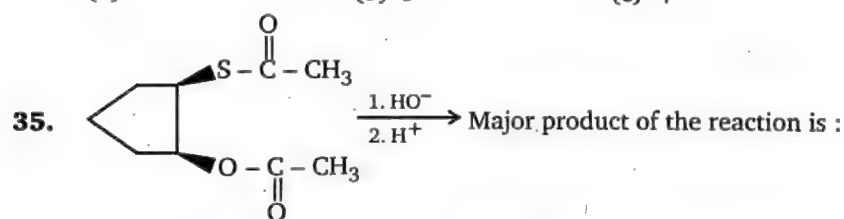
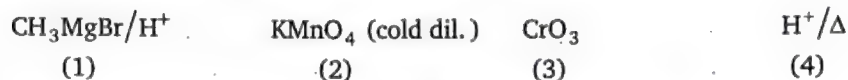
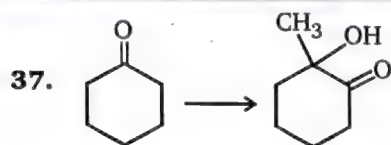
(d)

36.

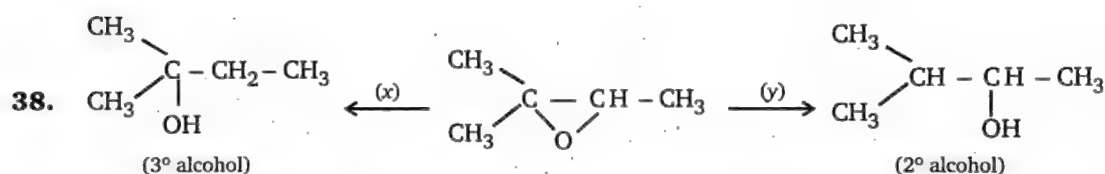
(c)

(d)

37. O (cyclohexanone) $\longrightarrow$ CH_3 OH, O (ring)

CH_3MgBr/H^+	$KMnO_4$ (cold dil.)	CrO_3	H^+/Δ
(1)	(2)	(3)	(4)

For the above conversion the correct order of reagents used is :

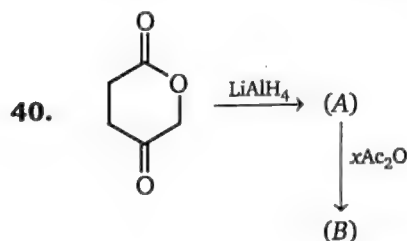
(a) $1 \to 2 \to 3 \to 4$ (b) $1 \to 4 \to 3 \to 2$
(c) $1 \to 4 \to 2 \to 3$ (d) $2 \to 3 \to 4 \to 1$

38. $(CH_3)_2C(OH)-CH_2-CH_3$ (3° alcohol) $\xleftarrow{(x)}$ $(CH_3)_2\overset{O}{C-CH}-CH_3$ $\xrightarrow{(y)}$ $(CH_3)_2CH-CH(OH)-CH_3$ (2° alcohol)

Find missing reagents.

(a) $x = LiAlH_4, y = NaBH_4$ (b) $x = LiAlH_4/AlCl_3, y = LiAlH_4$
(c) $x = LiAlH_4, y = LiAlH_4/AlCl_3$ (d) $x = H_2/Ni, y = H_2/Pt$

39. In solvolysis of 1, 2-dimethyl propyl p-toluene sulfonate in acetic acid at 75°C, (alkene + substitution products) will be formed by mechanism ?

(a) S_{N^2}, E_2 (b) S_{N^2}, E_1 (c) S_{N^1}, E_2 (d) S_{N^1}, E_1

40.

x = moles of anhydride consumed

(a) 1 (b) 2 (c) 3 (d) 4

41. Identify product when (*R*) – and (*S*) – 2 – butanol reacts with (*R*,*R*) tartaric acid in acidic medium.

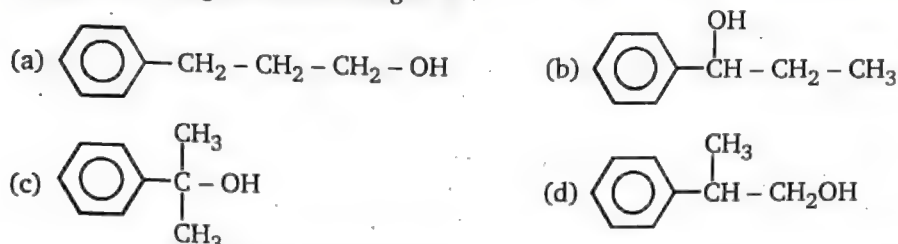
(a) Racemic (b) Diastereomer
(c) Meso (d) Pure enantiomer

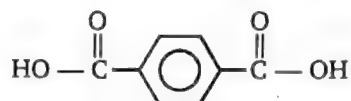
42. An alcohol of formula $C_9H_{12}O$ reacts with $Na_2Cr_2O_7$ to form a compound having formula $C_9H_{10}O$. The original alcohol might be :

(a) $C_6H_5-CH_2-CH_2-CH_2-OH$

(b) $C_6H_5-CH(OH)-CH_2-CH_3$

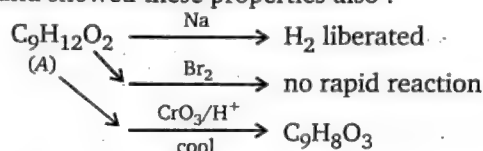
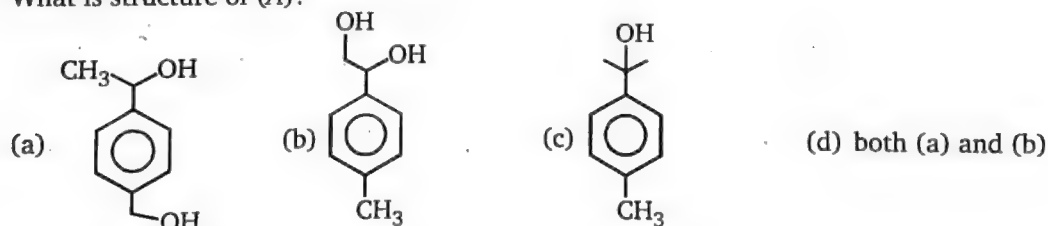
(c) $C_6H_5-C(CH_3)_2-OH$

(d) $C_6H_5-CH(CH_3)-CH_2OH$

43. An optically active alcohol of formula $C_9H_{12}O_2$ produced the following compound when refluxed with $KMnO_4$.

$$HO-\overset{O}{\overset{||}{C}}-C_6H_4-\overset{O}{\overset{||}{C}}-OH$$

The original compound showed these properties also :

$$C_9H_{12}O_2\ (A) \xrightarrow{Na} H_2 \text{ liberated}$$
$$C_9H_{12}O_2\ (A) \xrightarrow{Br_2} \text{no rapid reaction}$$
$$C_9H_{12}O_2\ (A) \xrightarrow[\text{cool}]{CrO_3/H^+} C_9H_8O_3$$

What is structure of (A)?

(a) p-$(CH_3CH(OH))C_6H_4CH_2OH$ (b) p-$(HOCH_2CH(OH))C_6H_4CH_3$ (c) p-$((CH_3)_2C(OH))C_6H_4CH_3$ (d) both (a) and (b)

44. Which are not cleaved by HIO_4?

I : glycerol
II : glycol
III : 1, 3-propenediol
IV : methoxy-2-propanol

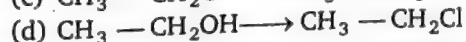
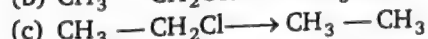
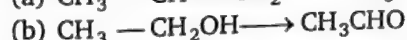
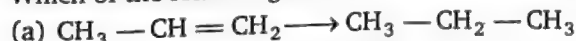
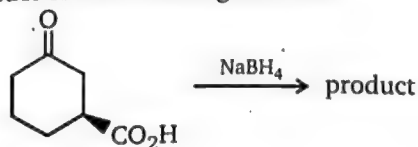
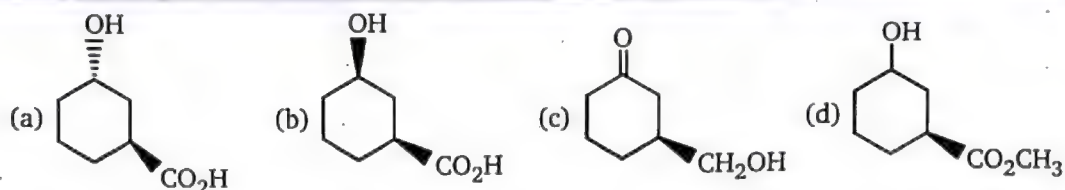
(a) I, II, III, IV
(b) I, II
(c) II, III
(d) III, IV

45. Which of the following reactions require an oxidising agent ?

(a) $CH_3-CH=CH_2 \longrightarrow CH_3-CH_2-CH_3$
(b) $CH_3-CH_2OH \longrightarrow CH_3CHO$
(c) $CH_3-CH_2Cl \longrightarrow CH_3-CH_3$
(d) $CH_3-CH_2OH \longrightarrow CH_3-CH_2Cl$

46. What is the major product of the following reaction ?

3-oxocyclohexane (with wedge CO_2H) $\xrightarrow{NaBH_4}$ product

(a) [cyclohexane with OH (hashed) and CO_2H (wedge)] (b) [cyclohexane with OH (wedge) and CO_2H (wedge)] (c) [cyclohexanone with CH_2OH (wedge)] (d) [cyclohexane with OH and CO_2CH_3 (wedge)]

47. Which of the esters shown, after reduction with $LiAlH_4$ and aqueous workup, will yield two molecules of only a single alcohol ?

(a) $CH_3CH_2CO_2CH_2CH_3$ (b) $C_6H_5CO_2CH_2C_6H_5$
(c) $C_6H_5CO_2C_6H_5$ (d) None of these

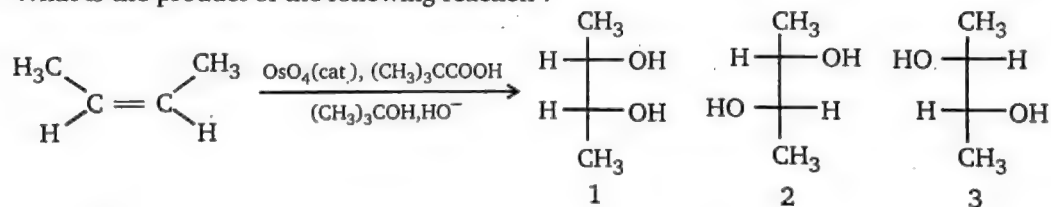
48. For the following reaction, select the statement that best describes the change.

$$RCH_2OH + PCC\ [C_5H_5NH^+ClCrO_3^-] \longrightarrow$$

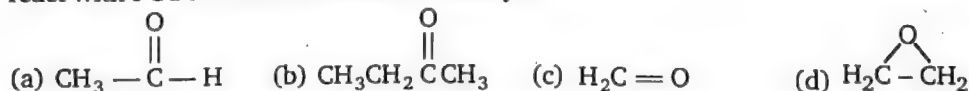
(a) The alcohol is oxidized to an acid, and the Cr(VI) is reduced
(b) The alcohol is oxidized to an aldehyde, and the Cr(VI) is reduced
(c) The alcohol is reduced to an aldehyde, and the Cr(III) is oxidized
(d) The alcohol is oxidized to a ketone, and the Cr(VI) is reduced

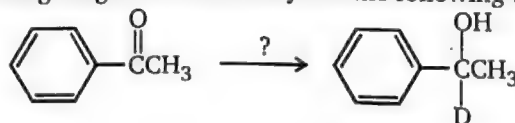
49. What is the product of the following reaction ?

$H_3C(H)C=C(H)CH_3$ $\xrightarrow[(CH_3)_3COH, HO^-]{OsO_4(cat.), (CH_3)_3CCOOH}$

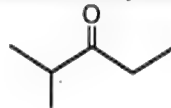
1: CH_3; H—OH; H—OH; CH_3
2: CH_3; H—OH; HO—H; CH_3
3: CH_3; HO—H; H—OH; CH_3

(a) Only 1 (b) 1 : 1 mixture of 2 and 3
(c) Only 2 (d) 1 : 1 : 1 mixture of 1, 2, and 3

50. An organic compound *B* is formed by the reaction of ethylmagnesium iodide (CH_3CH_2MgI) with a substance *A*, followed by treatment with dilute aqueous acid. Compound B does not react with PCC in dichloromethane. Identify *A* ?

(a) $CH_3-\overset{O}{\overset{\|}{C}}-H$ (b) $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$ (c) $H_2C=O$ (d) H_2C-CH_2 (epoxide, O bridging)

51. Which of the following reagents would carry out the following transformation ? (D = ²H)

$C_6H_5-\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{?} C_6H_5-C(OH)(D)CH_3$

(a) $NaBD_4$ in CH_3OH (b) $LiAlH_4$, then D_2O
(c) $NaBD_4$ in CH_3OD (d) $LiAlD_4$, then D_2O

52. Which sequence of steps describes the best synthesis of 2-methyl-3-pentanone ?

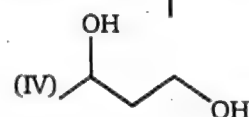
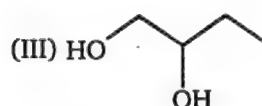
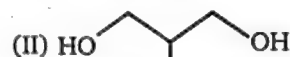
[skeletal structure of 2-methyl-3-pentanone]

(a) (1) 1-Propanol + $(CH_3)_2CHMgBr$, diethyl ether
 (2) H_3O^+
 (3) PCC, CH_2Cl_2

(b) (1) 1-Propanol + $Na_2Cr_2O_7$, H_2SO_4, H_2O, heat
 (2) $SOCl_2$
 (3) $(CH_3)_2CHCl$, $AlCl_3$

(c) (1) 1-Propanol + PCC, CH_2Cl_2
 (2) $(CH_3)_2CHLi$, diethyl ether
 (3) H_3O^+
 (4) $Na_2Cr_2O_7, H_2SO_4, H_2O$, heat

(d) (1) 2-Propanol + $Na_2Cr_2O_7$, H_2SO_4, H_2O, heat
 (2) $CH_3CH_2CH_2Li$, diethyl ether
 (3) H_3O^+
 (4) PCC, CH_2Cl_2

53. Diols (I-IV) which react with CrO_3 in aqueous H_2SO_4 and yield products that readily under go dercarboxylation on heating, are :

(I) HO～～OH (II) HO～～OH (III) HO～～(OH) (IV) (OH)～～OH

(a) I and II (b) II and III (c) II and IV (d) I and IV

54. Which of following compounds are not oxidized by HIO_4?

(1) $CH_3-CH(OH)-CH_2-OH$

(2) $CH_3-C(=O)-C(=O)-H$

(3) $CH_3-C(=O)-C(=O)-CH_3$

(4) $CH_3-C(=O)-CH(NH_2)-CH_3$

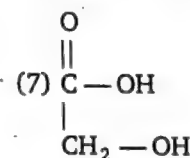
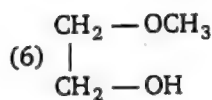
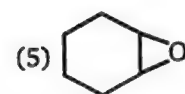
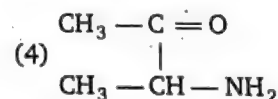
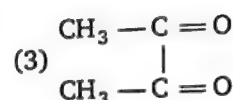
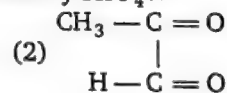
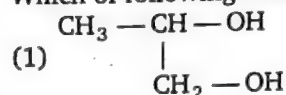
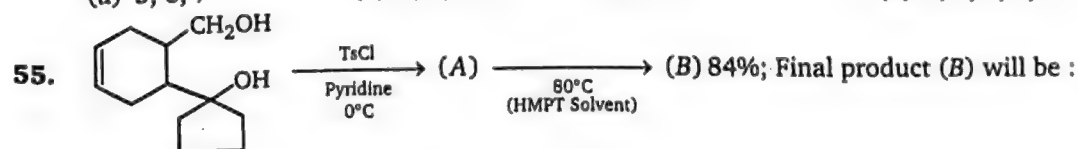
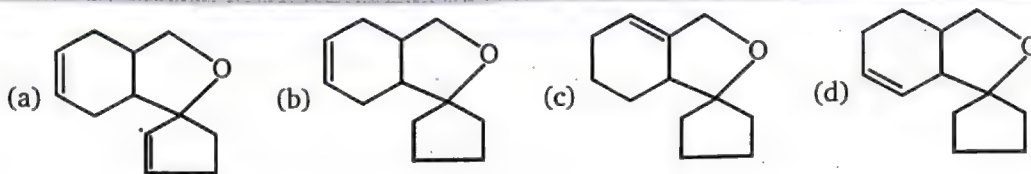
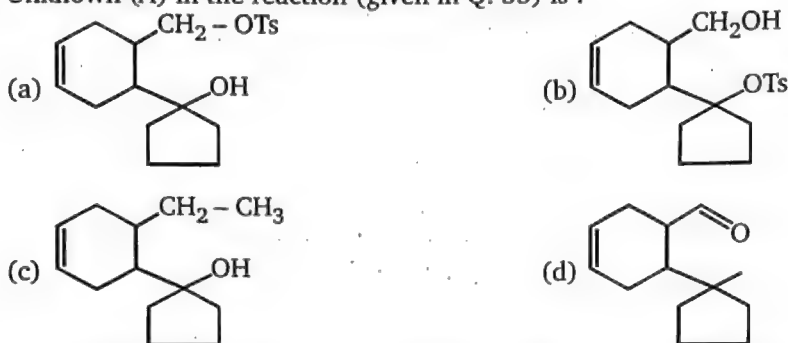
(5)

(6) $CH_2(OCH_3)-CH_2-OH$

(7) $HO-C(=O)-CH_2-OH$

(a) 5, 6, 7 (b) 4, 5, 6, 7 (c) 6, 7 (d) 3, 4, 5, 6, 7

55.

$\xrightarrow[\text{Pyridine, } 0°C]{TsCl}$ (A) $\xrightarrow[\text{(HMPT Solvent)}]{80°C}$ (B) 84%; Final product (B) will be :

56. Unknown (*A*) in the reaction (given in Q. 55) is :

57. In the given table, identify the incorrect option. The digit in box indicate the moles of that substance.

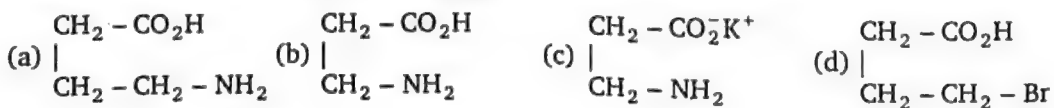
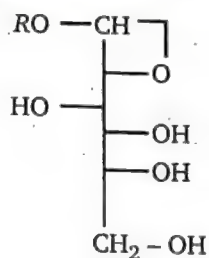
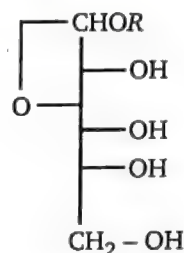
	Reactant	HIO_4 consumed	HCO_2H formed	HCHO formed
(a)	$HO-CH_2-\underset{\vert}{\overset{OH}{CH}}-CH_2-OH$	2	1	2
(b)	$R-\overset{OH}{CH}-\overset{OH}{CH}-\overset{OH}{CH}-CH_2-OH$	3	2	1
(c)	$HO-CH_2-\overset{OCH_3}{CH}-CH_2OH$	0	0	0
(d)	$HO-CH_2-\overset{OH}{CH}-\overset{OCH_3}{CH_2}$	1	1	1

58. Succinic acid $\xrightarrow{\Delta}(A)\xrightarrow[\Delta]{NH_3}(B)\xrightarrow[KOH]{Br_2}(C)$; Product (*C*) will be :

(a) $\begin{array}{l} CH_2-CO_2H \\ \vert \\ CH_2-CH_2-NH_2 \end{array}$

(b) $\begin{array}{l} CH_2-CO_2H \\ \vert \\ CH_2-NH_2 \end{array}$

(c) $\begin{array}{l} CH_2-CO_2^-K^+ \\ \vert \\ CH_2-NH_2 \end{array}$

(d) $\begin{array}{l} CH_2-CO_2H \\ \vert \\ CH_2-CH_2-Br \end{array}$

59A. Given are the structures of cyclic D-glucoside. Moles of HIO_4 consumed with X and Y are .... respectively:

(a) 2, 2
(b) 3, 3
(c) 2, 3
(d) 3, 2

B. Moles of formic acid formed in X and Y respectively are:
(a) 1, 2
(b) 2, 1
(c) 2, 3
(d) 3, 2

C. Moles of HCHO formed are:
(a) 1, 1
(b) 2, 2
(c) 1, 2
(d) 2, 1

60. In which of the following group, each member gives positive iodoform test ?
(a) methanol, ethanol, propanone
(b) ethanol, isopropanal, methanal
(c) ethanol, ethanal, isopropyl alcohol
(d) propanal, propanol-2, propanone

61. $H_2O^{18} + Na \longrightarrow \underset{\text{(base)}}{(A)} + (B)$

$$CH_3 - \overset{\overset{O}{||}}{C} - O - CH_2 - CH_3 + (A) \longrightarrow (C) + (D) \text{ alcohol}$$

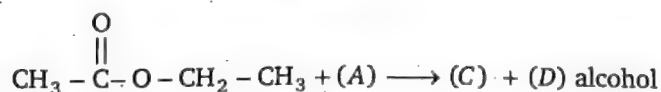
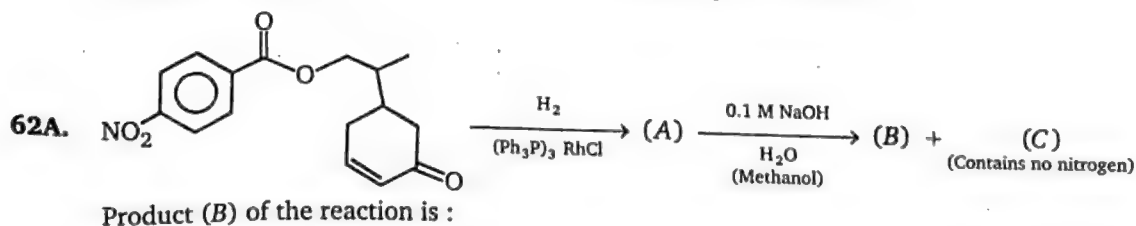
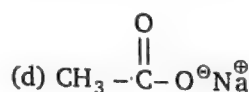
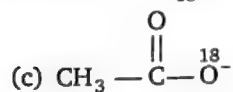
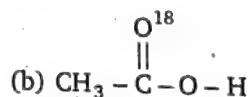
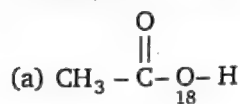
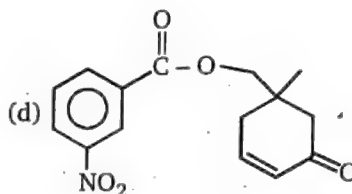
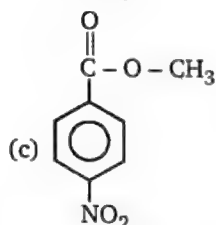
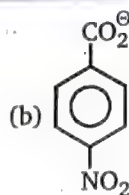
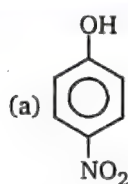
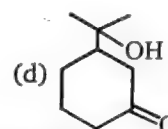
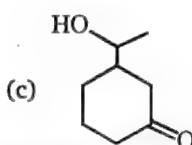
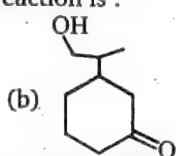
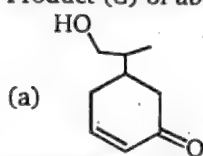
Product (C) of the reactions is:

(a) $CH_3 - \overset{\overset{O}{||}}{C} - \underset{18}{O} - H$
(b) $CH_3 - \overset{\overset{O^{18}}{||}}{C} - O - H$
(c) $CH_3 - \overset{\overset{O}{||}}{C} - \overset{18}{O^-}$
(d) $CH_3 - \overset{\overset{O}{||}}{C} - O^{\ominus}\overset{\oplus}{Na}$

62A.

Product (B) of the reaction is :

(a) [benzene ring with OH and NO_2 para] (b) [benzene ring with $CO_2^{\ominus}$ and NO_2 para]

(c) [benzene ring with $-\overset{O}{\overset{||}{C}}-O-CH_3$ and NO_2 para] (d) [m-nitrobenzene ring with $-\overset{O}{\overset{||}{C}}-O-$ linked to cyclohexenone ring]

B. Product (*C*) of above reaction is :

63. Two unknown compounds *X* and *Y*, both having molecular formula C_4H_8O, give following results with four chemical tests.

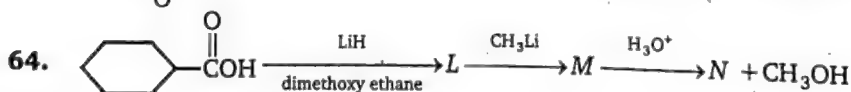
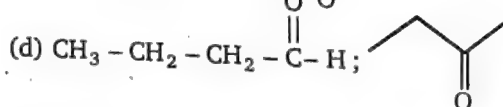
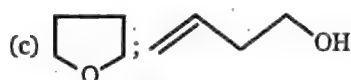
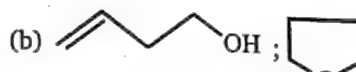
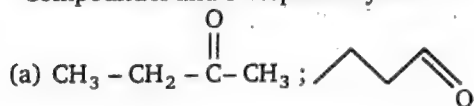
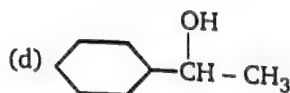
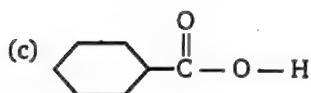
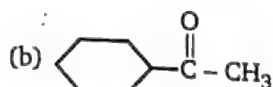
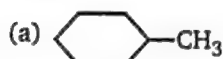
	Bromine	Na metal	Chromic acid	Lucas reagent
Compound *X*	decolourises	bubbles	Orange to Green	No reaction
Compound *Y*	No reaction	No reaction	No reaction	No reaction

Compound *X* and *Y* respectively are :

64. [cyclohexane]$-\overset{O}{\overset{||}{C}}OH \xrightarrow[\text{dimethoxy ethane}]{LiH} L \xrightarrow{CH_3Li} M \xrightarrow{H_3O^+} N + CH_3OH$

Product (*N*) is :

(a) [cyclohexane]$-CH_3$ (b) [cyclohexane]$-\overset{O}{\overset{||}{C}}-CH_3$

(c) [cyclohexane]$-\overset{O}{\overset{||}{C}}-O-H$ (d) [cyclohexane]$-\overset{OH}{\overset{|}{C}H}-CH_3$

65. Assign the structure of major product (X) of the reaction given below.

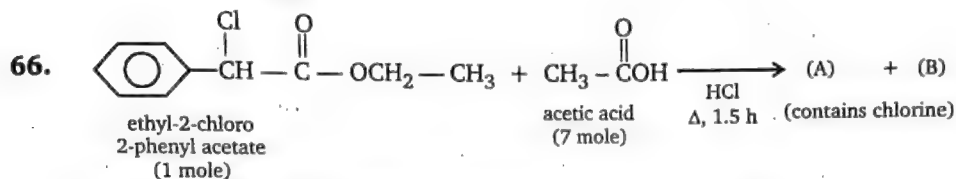
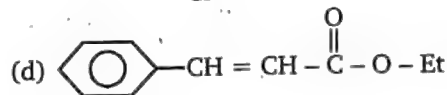
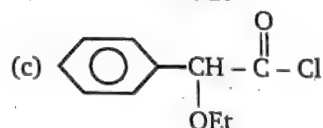
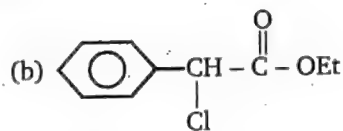
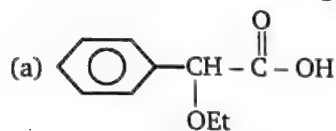
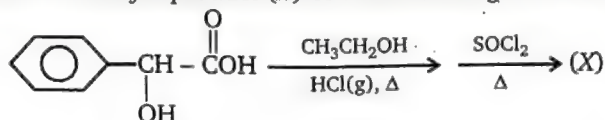
$$C_6H_5-\underset{OH}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}OH \xrightarrow[HCl(g),\ \Delta]{CH_3CH_2OH} \xrightarrow[\Delta]{SOCl_2} (X)$$

(a) $C_6H_5-\underset{OEt}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-OH$

(b) $C_6H_5-\underset{Cl}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-OEt$

(c) $C_6H_5-\underset{OEt}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-Cl$

(d) $C_6H_5-CH=CH-\overset{O}{\overset{||}{C}}-O-Et$

66. $$\underset{\substack{\text{ethyl-2-chloro}\\ \text{2-phenyl acetate}\\ \text{(1 mole)}}}{C_6H_5-\overset{Cl}{\overset{|}{CH}}-\overset{O}{\overset{||}{C}}-OCH_2-CH_3} + \underset{\substack{\text{acetic acid}\\ \text{(7 mole)}}}{CH_3-\overset{O}{\overset{||}{C}}OH} \xrightarrow[\Delta,\ 1.5\ h]{HCl} \underset{\text{(contains chlorine)}}{(A)} + (B)$$

Product (A) and (B) respectively in the above reaction are :

(a) $C_6H_5-\underset{Cl}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-OH,\ CH_3-\overset{O}{\overset{||}{C}}-OCH_2CH_3$

(b) $C_6H_5-\underset{Cl}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-OEt,\ CH_3-\overset{O}{\overset{||}{C}}-OCH_3$

(c) $C_6H_5-\underset{Cl}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-OEt,\ CH_3-\overset{O}{\overset{||}{C}}-OH$

(d) $C_6H_5-CH_2-Cl,\ CH_3-\overset{O}{\overset{||}{C}}-OH$

67. $$\underset{\substack{\text{methylacrylate}\\ \text{bpt } 81^\circ C}}{H_2C=CH-\overset{O}{\overset{||}{C}}-OCH_3} + \underset{\substack{n\text{-butyl alcohol}\\ \text{bpt } 117^\circ C}}{CH_3CH_2CH_2OH} \xrightarrow{TsOH,\ \Delta} \underset{\text{bpt},145^\circ C}{(A)} + \underset{\text{bpt } 65^\circ C}{CH_3OH}$$

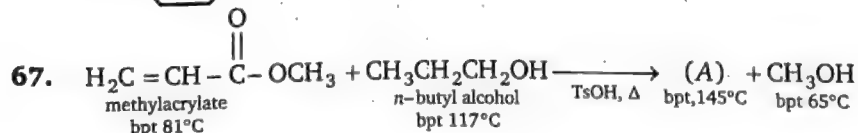
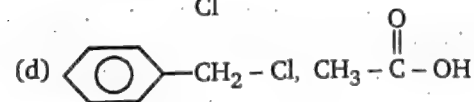
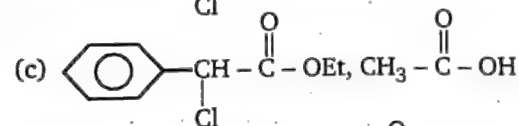
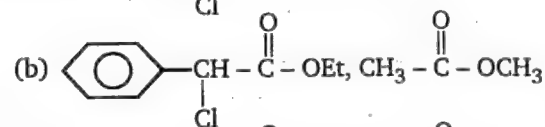
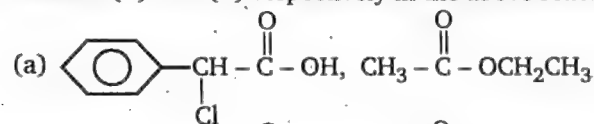
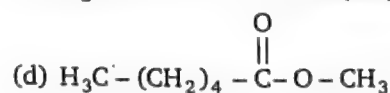
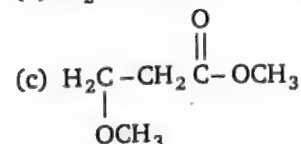
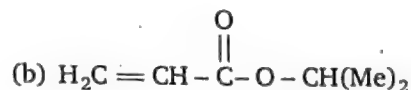
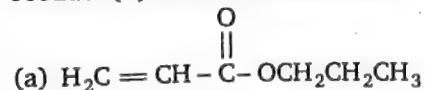
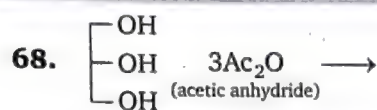
Product (A) of above reaction is :

(a) $H_2C=CH-\overset{O}{\overset{||}{C}}-OCH_2CH_2CH_3$

(b) $H_2C=CH-\overset{O}{\overset{||}{C}}-O-CH(Me)_2$

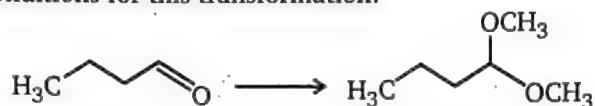
(c) $H_2\underset{OCH_3}{\underset{|}{C}}-CH_2\overset{O}{\overset{||}{C}}-OCH_3$

(d) $H_3C-(CH_2)_4-\overset{O}{\overset{||}{C}}-O-CH_3$

68. $-OH$, $-OH$, $-OH$ (glycerol) $\xrightarrow{3Ac_2O\ \text{(acetic anhydride)}}$

In above reaction molecular formula of glycerol increases by :

(a) $C_4H_4O_2$ (b) $C_6H_6O_6$ (c) $C_6H_6O_2$ (d) $C_6H_6O_3$

69. Give the best conditions for this transformation:

H_3C–CH_2–CH_2–CHO ⟶ H_3C–CH_2–CH_2–$CH(OCH_3)OCH_3$

(a) CH_3OH, H^+ (cat.), heat (b) H_2O, H^+ (cat.), heat

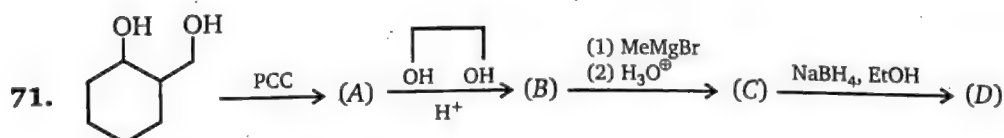
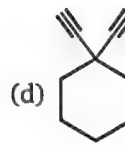
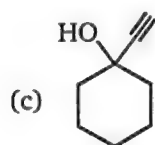
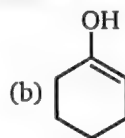
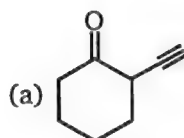
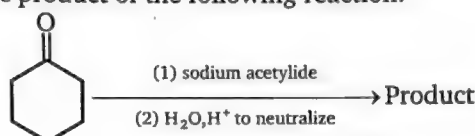
(c) Mg, ether, CH_3OH (d) $SOCl_2, CH_3OH$

70. Give the major organic product of the following reaction.

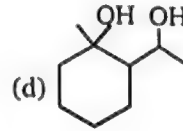
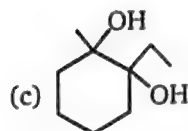
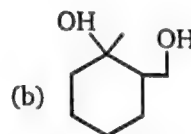
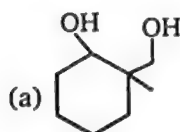
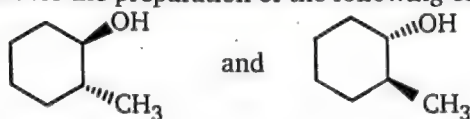
Cyclohexanone $\xrightarrow[\text{(2) } H_2O, H^+ \text{ to neutralize}]{\text{(1) sodium acetylide}}$ Product

(a) (b) (c) HO (d)

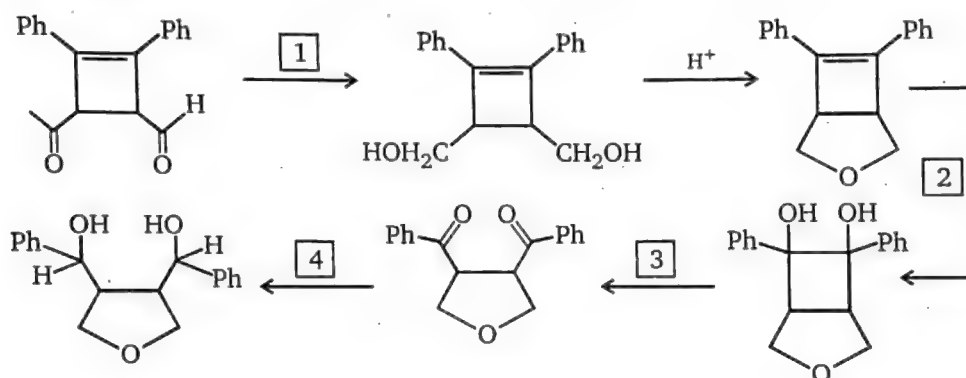
(b) OH

71. OH OH $\xrightarrow{PCC}$ (A) $\xrightarrow[H^+]{OH\quad OH}$ (B) $\xrightarrow{\text{(1) MeMgBr, (2) } H_3O^{\oplus}}$ (C) $\xrightarrow{NaBH_4,\ EtOH}$ (D)

Product (D) in above reaction is :

(a) OH OH (b) OH OH

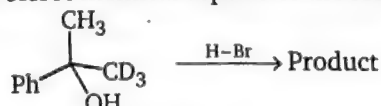
(c) OH OH (d) OH OH

72. Select the best method for the preparation of the following compounds :

(MCPBA = Metachloro per benzoic acid)

(a) reaction of cyclohexanone with CH_3Li
(b) reaction of 1-methylcyclohexene with $Hg(OAc)_2$ followed by $NaBH_4$
(c) reaction of cyclohexene with $BH_3; NaOH/H_2O_2$, following by CH_3Br
(d) reaction of cyclohexene with MCPBA, followed by CH_3MgBr

73. Identify the reagents (1-4), required for the transformations shown and arrange them in correct order.

(1) LAH ($LiAlH_4$)
(2) OsO_4
(3) $NaIO_4$
(4) $NaBH_4$

(a) $1 \rightarrow 3 \rightarrow 4 \rightarrow 2$
(b) $2 \rightarrow 3 \rightarrow 1 \rightarrow 4$
(c) $2 \rightarrow 1 \rightarrow 3 \rightarrow 4$
(d) $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$

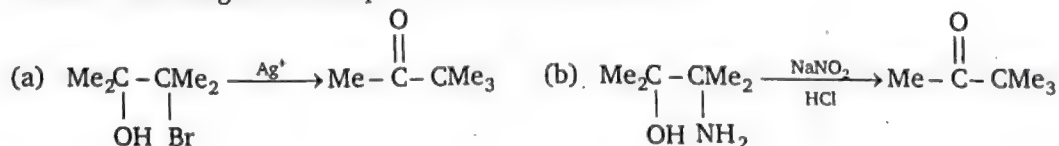
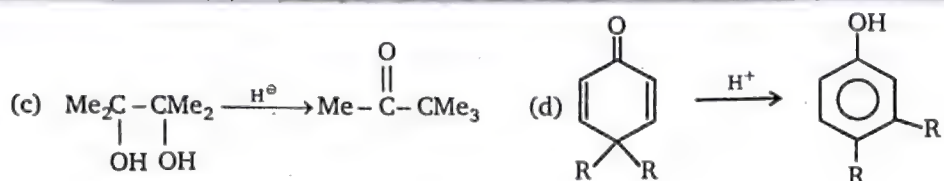
74. Which describes the best stereochemical aspects of the following reaction ?

$$Ph-C(CH_3)(CD_3)(OH) \xrightarrow{H-Br} \text{Product}$$

(a) Inversion of configuration occurs at the carbon undergoing substitution.
(b) Retention of configuration occurs at the carbon undergoing substitution.
(c) Racemization (loss of configuration) occurs at the carbon undergoing substitution.
(d) The carbon undergoing substitution is not stereogenic

75. Which of following is an example of Pinacol-Diazotization ?

(a) $Me_2C(OH)-CMe_2(Br) \xrightarrow{Ag^+} Me-\overset{O}{\overset{||}{C}}-CMe_3$

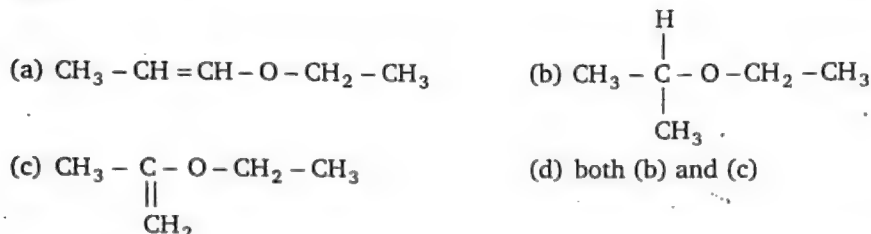
(b) $Me_2C(OH)-CMe_2(NH_2) \xrightarrow[HCl]{NaNO_2} Me-\overset{O}{\overset{||}{C}}-CMe_3$

(c) $Me_2\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}Me_2 \xrightarrow{H^{\oplus}} Me-\overset{O}{\overset{||}{C}}-CMe_3$ (d) 4,4-dialkyl cyclohexa-2,5-dienone (R, R) $\xrightarrow{H^+}$ phenol (OH) with R, R substituents

76. $\underset{C_5H_{10}O}{(A)} \xrightarrow{H_3O^{\oplus}} B+C$; (B) and (C) both give +ve iodoform test. Compound (A) is :

(a) $CH_3-CH=CH-O-CH_2-CH_3$

(b) $CH_3-\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}-O-CH_2-CH_3$

(c) $CH_3-\underset{CH_2}{\underset{||}{C}}-O-CH_2-CH_3$

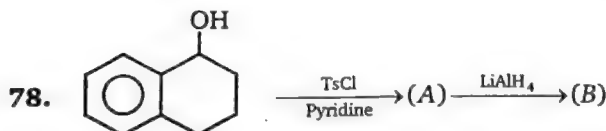
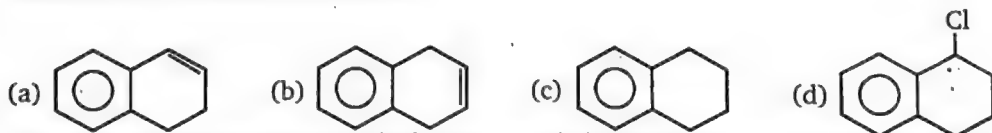
(d) both (b) and (c)

77. A solution of Ph_3CCO_2H in conc. H_2SO_4 gives (X) when poured into methanol X is :

(a) $Ph_3C-\overset{O}{\overset{||}{C}}-O-CH_3$

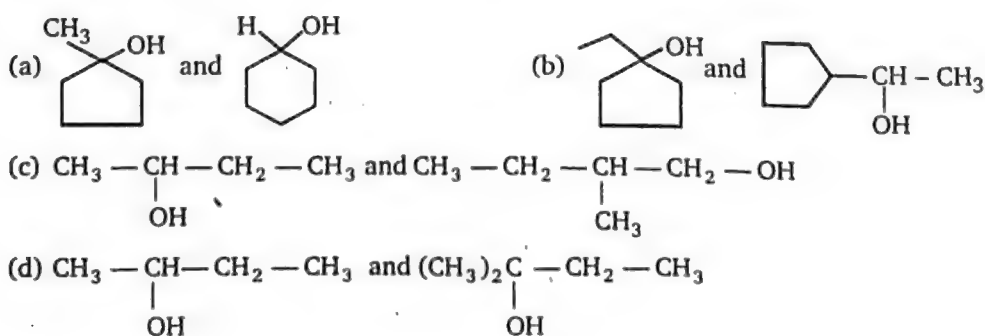
(b) $Ph_2CH-\overset{O}{\overset{||}{C}}-O-CH_3$

(c) Ph_3C-OCH_3

(d) Ph_3C-CH_3

78.

Product (B) of the above reaction is :

79. In the given pair of alcohol, in which pair second alcohol is more reactive than first towards hydrogen bromide?

(c) $CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$ and $CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-OH$

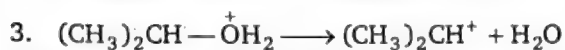
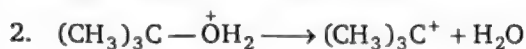
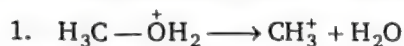
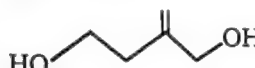
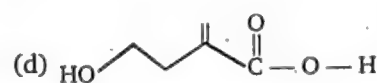
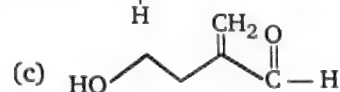
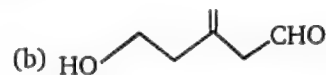
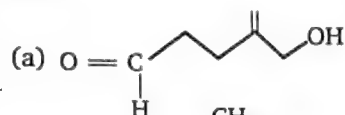
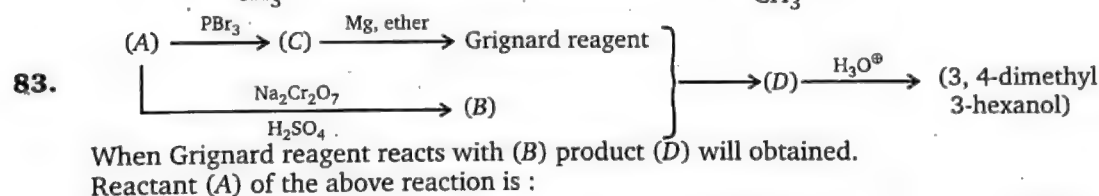
(d) $CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$ and $(CH_3)_2\underset{OH}{\underset{|}{C}}-CH_2-CH_3$

80. Rank the transition states that occur during the following reaction steps in order of increasing stability (least → most stable)

1. $H_3C-\overset{+}{O}H_2 \longrightarrow CH_3^+ + H_2O$
2. $(CH_3)_3C-\overset{+}{O}H_2 \longrightarrow (CH_3)_3C^+ + H_2O$
3. $(CH_3)_2CH-\overset{+}{O}H_2 \longrightarrow (CH_3)_2CH^+ + H_2O$

(a) $1 < 2 < 3$ (b) $2 < 3 < 1$ (c) $1 < 3 < 2$ (d) $2 < 1 < 3$

81. HO⁄⁄OH $\xrightarrow{MnO_2}$ (A), Product (A) is :

(a) $O=\underset{H}{C}$ ⁄⁄OH (b) HO ⁄⁄CHO

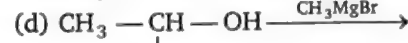
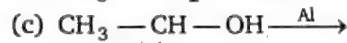
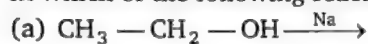
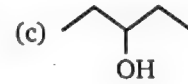
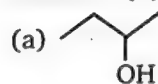
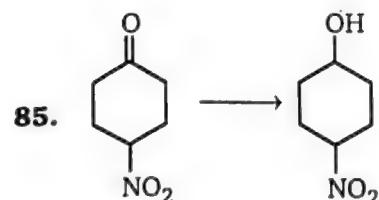
(c) HO ⁄⁄ CH_2 O $\overset{\|}{C}-H$ (d) HO ⁄⁄ $\overset{O}{\overset{\|}{C}}-O-H$

82. In which of the following reactions hydrogen gas will not be evolved ?

(a) $CH_3-CH_2-OH \xrightarrow{Na}$ (b) $CH_3-CH_2-OH \xrightarrow{K}$

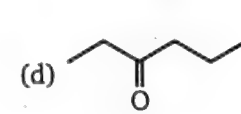
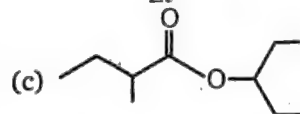
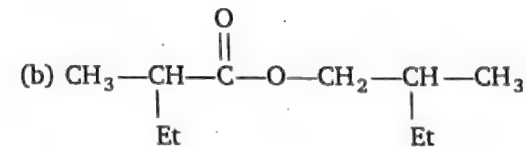
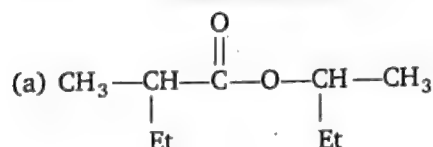
(c) $CH_3-\underset{CH_3}{\underset{|}{CH}}-OH \xrightarrow{Al}$ (d) $CH_3-\underset{CH_3}{\underset{|}{CH}}-OH \xrightarrow{CH_3MgBr}$

83. $(A) \xrightarrow{PBr_3} (C) \xrightarrow{Mg,\ ether}$ Grignard reagent ; $(A) \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} (B)$; Grignard reagent + $(B) \longrightarrow (D) \xrightarrow{H_3O^{\oplus}}$ (3, 4-dimethyl 3-hexanol)

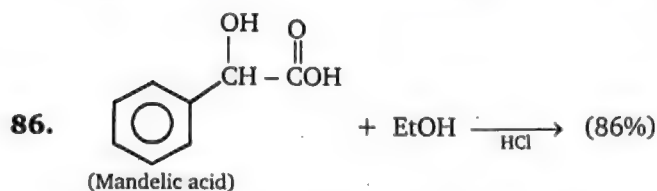
When Grignard reagent reacts with (B) product (D) will obtained.
Reactant (A) of the above reaction is :

(a) OH (b) OH (c) OH (d) OH

84. $(A) \xrightarrow{LiAlH_4} \underset{\text{(Chiral alcohol only)}}{2(B)}$; structure of (A) is :

(d) O

85. O, NO_2 $\longrightarrow$ OH, NO_2

Above conversion can be acheived by :

(a) $LiAlH_4$ (b) $NaBH_4$ (c) H_2/Ni (d) CrO_3

86. (Mandelic acid) $C_6H_5-CH(OH)-\overset{O}{\overset{||}{C}}OH$ + EtOH $\xrightarrow{HCl}$ (86%)

Identify product of above Fischer esterification reaction :

(a) $Ph-CH(O-Et)-CO_2H$

(b) $Ph-\overset{O}{CH-C}=O$ (epoxide)

(c) $Ph-CH(OH)-CO_2Et$

(d) $Ph-CH(OH)-\overset{O}{\overset{||}{C}}-Et$

87. CH_3 / $CH_2CH_2\overset{O}{\overset{||}{C}}OH$ (ethylene ketal, 1,3-dioxolane) $\xrightarrow{CH_3Li} (A) \xrightarrow{CH_3Li} (B) \xrightarrow{H_3O^{\oplus}} (C)$

Product (*C*) of the above reaction is :

(a) $CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_2-\overset{OH}{\overset{|}{C}}(CH_3)-CH_3$

(b) $CH_3-\overset{OH}{\overset{|}{C}}(CH_3)-CH_2-CH_2-\overset{OH}{\overset{|}{C}}(CH_3)-CH_3$

(c) $CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_2-\overset{O}{\overset{||}{C}}-CH_3$

(d) $CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-CH_3$

88. What is the major product of the following reaction ?

$CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-CH_2-OH \xrightarrow[\text{Pyridine cold}]{CrO_3}$ Product

(a) $CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{||}{C}}-H$

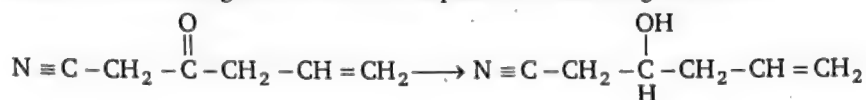
(b) $CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-H$

(c) $CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-OH$

(d) $CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{||}{C}}-OH$

89. The major reason that phenol is a better Bronsted acid than cyclohexanol is that :
(a) it is a better proton donor.
(b) the cyclohexyl group is an electron donating group by induction, which destabilizes the anion formed in the reaction by resonance.
(c) phenol is able to stabilize the anion formed in the reaction.
(d) the phenyl group is an electron withdrawing group by induction, which stabilizes the anion formed in the reaction.

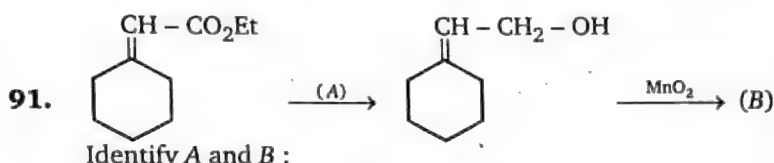
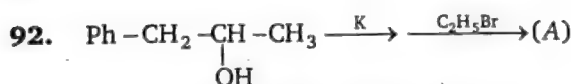
90. Which of these reagents would accomplish the following reduction ?

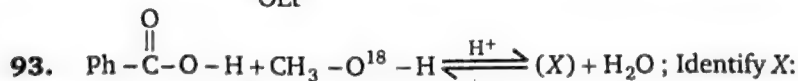
$$N \equiv C-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH=CH_2 \longrightarrow N \equiv C-CH_2-\underset{H}{\overset{OH}{\overset{|}{C}}}-CH_2-CH=CH_2$$

(a) $NaBH_4$ (b) $LiAlH_4$
(c) 1 mole H_2, poisoned catalyst, low pressure (d) H_3O^+

91. Cyclohexylidene$=CH-CO_2Et$ $\xrightarrow{(A)}$ Cyclohexylidene$=CH-CH_2-OH$ $\xrightarrow{MnO_2}$ (B)

Identify A and B :

(a) $A = NaBH_4$, $B =$ Cyclohexylidene$=CH-CO_2H$ (b) $A = NaBH_4$, $B =$ Cyclohexylidene$=CH-CHO$
(c) $A = LiAlH_4$, $B =$ Cyclohexylidene$=CH-CHO$ (d) $A = LiAlH_4$, $B =$ Cyclohexylidene$=CH-CO_2H$

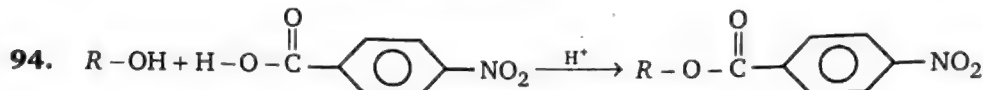
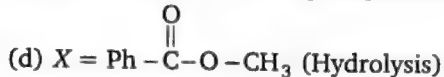
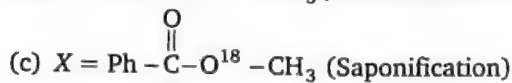
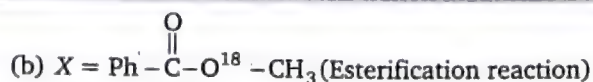
92. $Ph-CH_2-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow{K} \xrightarrow{C_2H_5Br} (A)$

Product (A) in above reaction is:
(a) $Ph-CH_2-\underset{OEt}{\underset{|}{CH}}-CH_3$, (inversion) (b) $Ph-CH_2-\underset{OEt}{\underset{|}{CH}}-CH_3$, (retention)
(c) $Ph-CH_2-\underset{OEt}{\underset{|}{CH}}-CH_3$, (racemic) (d) $Ph-CH=CH-CH_3$

93. $Ph-\overset{O}{\overset{\|}{C}}-O-H+CH_3-O^{18}-H \overset{H^+}{\rightleftharpoons} (X)+H_2O$; Identify X:

(a) $X = Ph-\overset{O}{\overset{\|}{C}}-O^{18}-CH_3$ (Trans esterification)

(b) $X = Ph-\overset{O}{\overset{\|}{C}}-O^{18}-CH_3$ (Esterification reaction)

(c) $X = Ph-\overset{O}{\overset{\|}{C}}-O^{18}-CH_3$ (Saponification)

(d) $X = Ph-\overset{O}{\overset{\|}{C}}-O-CH_3$ (Hydrolysis)

94. $R-OH + H-O-\overset{O}{\overset{\|}{C}}-C_6H_4-NO_2 \xrightarrow{H^+} R-O-\overset{O}{\overset{\|}{C}}-C_6H_4-NO_2$

Fastest rate of reaction will be when R is :

(a) CH_3- (b) CH_3-CH_2 (c) $CH_3-\underset{CH_3}{\underset{|}{CH}}-$ (d) $CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-$

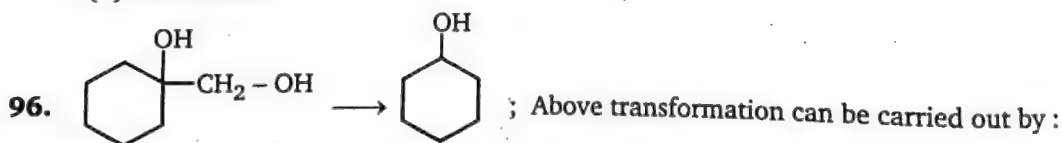
95. Select the correct statement.

(a) Solvolysis of $(CH_3)_2C=CH-CH_2-Cl$ in ethanol is over 6000 times greater than alkyl chloride (25°C)

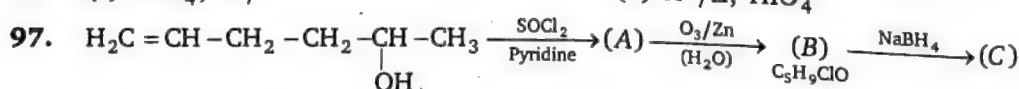
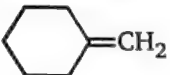
(b) $CH_3-CH=CH-CH_2-OH$ when reacts with HBr give a mixture of 1-bromo-2-butene and 3-bromo 1-butene

(c) When solution of 3-buten-2-ol in aqueous sulphuric acid is allowed to stand for one week, it was found to contain both 3-buten-2-ol and 2-buten-1-ol

(d) All of these

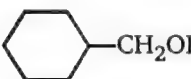
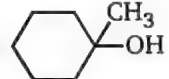
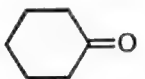
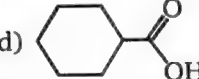
96. 1-(hydroxymethyl)cyclohexan-1-ol (ring C bearing OH and CH_2-OH) $\longrightarrow$ cyclohexanol (ring with OH) ; Above transformation can be carried out by :

(a) H^+/Δ, Zn(Hg), HCl (b) HIO_4, $LiAlH_4$

(c) HIO_4, H^+/Δ (d) H^+/Δ, HIO_4

97. $H_2C=CH-CH_2-CH_2-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{Pyridine}]{SOCl_2} (A) \xrightarrow[(H_2O)]{O_3/Zn} \underset{C_5H_9ClO}{(B)} \xrightarrow{NaBH_4} (C)$

Compound (C) is :

(a) $CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-\underset{Cl}{\underset{|}{CH}}-CH_3$

(b) $HOCH_2-CH_2-CH_2-CH_2-CH_2-CH_2-Cl$

(c) $HO-CH_2-CH_2-CH_2-\overset{Cl}{\overset{|}{CH}}-CH_3$

(d) $HO-CH_2-CH_2-\underset{Cl}{\underset{|}{CH}}-CH_2-CH_3$

98. Iodoform can be obtained on warming NaOH and iodine with :

(a) $CH_3CH_2CH(OH)CH_3$ (b) $(CH_3)_2CH\overset{O}{\overset{\|}{C}}C_2H_5$

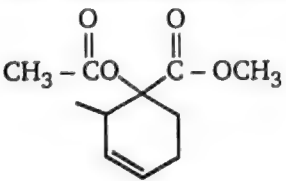
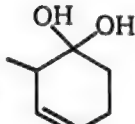
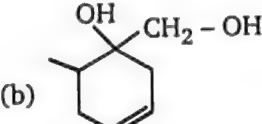
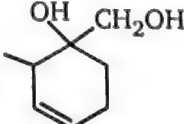
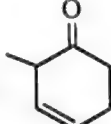
(c) $CH_3-\underset{O}{\underset{\|}{C}}-OCH_3$ (d) $(CH_3)_2CHCH_2OH$

99. Which of these is a reducing agent ?

(a) CrO_3/H^+ (b) $KMnO_4$

(c) $LiAlH_4$ (d) O_3

100. (cyclohexylidene)$=CH_2$ $\xrightarrow[\text{(ii). } H_2O_2/OH^-]{\text{(i). } (BH_3)_2}$ (P); Product (P) in the reaction is:

(a) (cyclohexyl)$-CH_2OH$ (b) (cyclohexane with CH_3 and $-OH$ on same carbon) (c) (cyclohexane)$=O$ (d) (cyclohexyl)$-C(=O)OH$

101. $CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 \xrightarrow[\text{cool}]{Na_2Cr_2O_7} (P)$; Product (P) in the reaction is:

(a) $CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2$ (b) $CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_3$

(c) $CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-O-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$ (d) No reaction

102. 1, 2, 3 – butanetriol undergoes oxidative cleavage of HIO_4. During this process

(a) 1 equivalent of HIO_4 consumed & HCO_2H & $H_3C-\underset{O}{\underset{\|}{C}}-CO_2H$ are formed

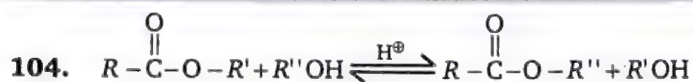
(b) 2 equivalents of HIO_4 consumed & HCO_2H, $HCH=O$ & $CH_3-CH=O$ are formed

(c) 3 equivalents of HIO_4 consumed & HCO_2H (2 eq.) & 1 eq. of CH_3CO_2H are formed

(d) 2 equivalents of HIO_4 consumed & 2 eq. of HCO_2H & 1 eq. of $CH_3CH=O$ is formed

103. (cyclohexene ring bearing methyl, with $CH_3-\overset{O}{\overset{\|}{C}}O$ and $\overset{O}{\overset{\|}{C}}-OCH_3$ on the same carbon) $\xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4}$ (A) (96%); Product (A) of the reaction is :

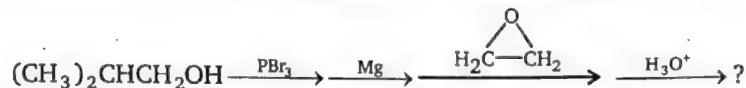
(a) (ring with OH, OH) (b) (ring with OH, CH_2-OH) (c) (ring with OH, CH_2OH) (d) (ring with $=O$)

104. $R-\overset{O}{\overset{\|}{C}}-O-R'+R''OH \underset{}{\overset{H^{\oplus}}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-O-R''+R'OH$

Above reaction is/an example of :

(a) esterification (b) saponification

(c) *trans*-esterification (d) hydrolysis

105. What is the major organic product of the following sequence of reactions ?

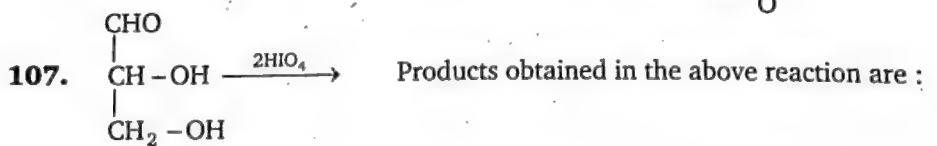
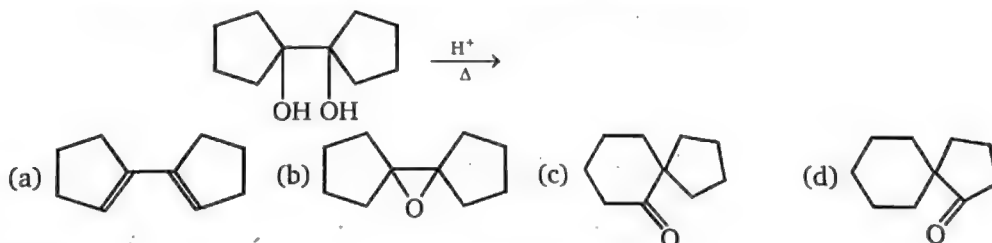
$(CH_3)_2CHCH_2OH \xrightarrow{PBr_3} \xrightarrow{Mg} \xrightarrow{H_2C\overset{O}{—}CH_2} \xrightarrow{H_3O^+} ?$

(a) $(CH_3)_2CH\overset{OH}{\overset{|}{C}H}CH_2CH_3$ (b) $(CH_3)_2CHCH_2CH_2OH$

(c) $(CH_3)_2CHCH_2\overset{OH}{\overset{|}{C}H}CH_3$ (d) $(CH_3)_2CHCH_2CH_2CH_2OH$

106. The structure of the product formed in the reaction given below is :

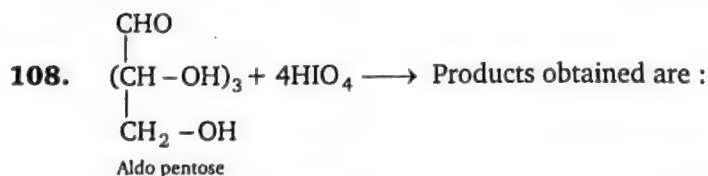
(reactant: two cyclopentane rings joined at carbons each bearing OH — OH OH) $\xrightarrow[\Delta]{H^+}$

(a) (b) (c) (d) O O O

107. $\begin{matrix} CHO \\ | \\ CH-OH \\ | \\ CH_2-OH \end{matrix} \xrightarrow{2HIO_4}$ Products obtained in the above reaction are :

(a) $HCHO, HCO_2H$ (b) $HCHO, 2HCO_2H$

(c) $CO_2, 2HCO_2H$ (d) $CO_2, HCHO, HCO_2H$

108. $\begin{matrix} CHO \\ | \\ (CH-OH)_3 \\ | \\ CH_2-OH \end{matrix} + 4HIO_4 \longrightarrow$ Products obtained are :

Aldo pentose

(a) $4HCO_2H$, HCHO (b) $4CH_2O$, HCO_2H

(c) CO_2, 4HCHO (d) $CO_2, 3HCO_2H$, HCHO

109. (i) $\begin{matrix} CHO \\ | \\ (CH-OH)_3 \\ | \\ CH_2-OH \end{matrix} \xrightarrow{4HIO_4}$ Product (ii) $\begin{matrix} CH_2OH \\ | \\ (CH-OH)_4 \\ | \\ CH_2-OH \end{matrix} \xrightarrow{5HIO_4}$ Product

Ratio of moles of formic acid obtained in reaction (i) and reaction (ii) is :

(a) 3/4 (b) 4/5 (c) 1 (d) 5/4

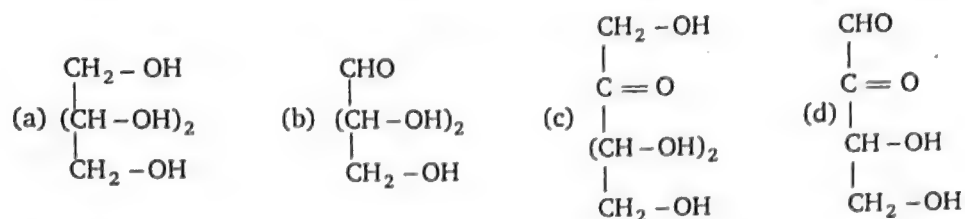
110. Which of the following compound gives $2HCHO, CO_2, HCO_2H$ when oxidised by periodic acid?

(a)

CH_2-OH | $(CH-OH)_2$ | CH_2-OH

(b) CHO | $(CH-OH)_2$ | CH_2-OH

(c) CH_2-OH | $C=O$ | $(CH-OH)_2$ | CH_2-OH

(d) CHO | $C=O$ | $CH-OH$ | CH_2-OH

111. Hydration of 3-phenylbut-1-ene in dil. H_2SO_4 will give mainly :

(a) 3-Phenylbutan-1-ol (b) 3-Phenylbutan-2-ol

(c) 2-Phenylbutan-2-ol (d) 2-Phenylbutan-1-ol

112. Decarboxylation of sodium salicylate with soda lime forms :

(a) Salicylic acid (b) Phenol (c) Benzene (d) None of these

113. MeO – CH(–CH–OH)–CH–OH–CH–OH–HC(–CH₂–OH), ring closed through O between MeO–CH and HC $\xrightarrow{xHIO_4}$ What is the maximum value of (x) ?

(a) 1 (b) 2 (c) 3 (d) 4

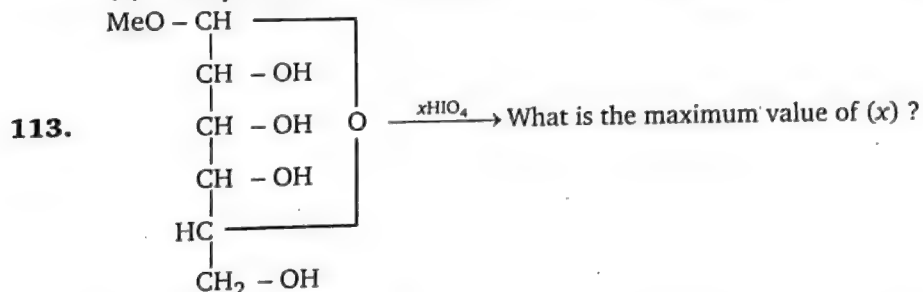
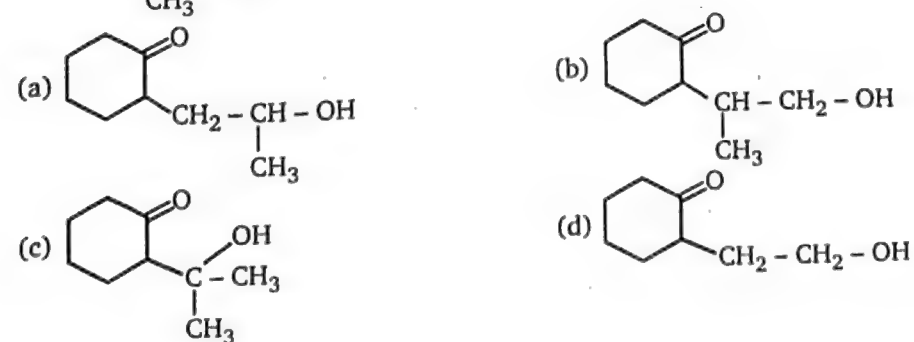
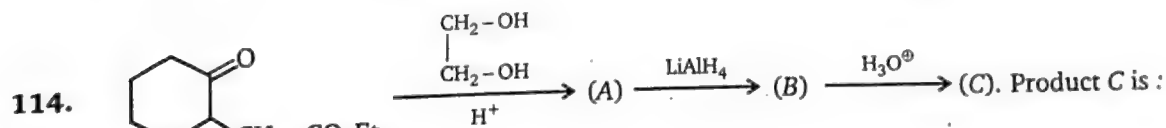
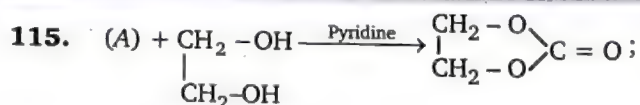
114. 2-($CH(CH_3)-CO_2Et$)cyclohexanone $\xrightarrow[H^+]{CH_2-OH \,|\, CH_2-OH}$ (A) $\xrightarrow{LiAlH_4}$ (B) $\xrightarrow{H_3O^{\oplus}}$ (C). Product C is :

(a) 2-($CH_2-CH(CH_3)-OH$)cyclohexanone

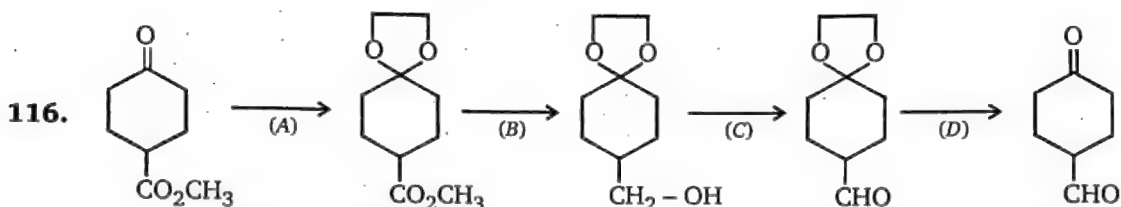
(b) 2-($CH(CH_3)-CH_2-OH$)cyclohexanone

(c) 2-($C(OH)(CH_3)-CH_3$)cyclohexanone

(d) 2-(CH_2-CH_2-OH)cyclohexanone

115. $(A) + \begin{matrix} CH_2-OH \\ | \\ CH_2-OH \end{matrix} \xrightarrow{\text{Pyridine}} \begin{matrix} CH_2-O \\ | \\ CH_2-O \end{matrix} \!\!> C = O$;

Reactant A of the above reaction is :

(a) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (b) $COCl_2$ (c) $CH_3-\overset{O}{\overset{\|}{C}}-Cl$ (d) $CH_3-\overset{O}{\overset{\|}{C}}-OEt$

116. (cyclohexanone with 4-CO_2CH_3) $\xrightarrow{(A)}$ (ethylene ketal, 4-CO_2CH_3) $\xrightarrow{(B)}$ (ethylene ketal, 4-CH_2-OH) $\xrightarrow{(C)}$ (ethylene ketal, 4-CHO) $\xrightarrow{(D)}$ (cyclohexanone with 4-CHO)

Identify correct combination :

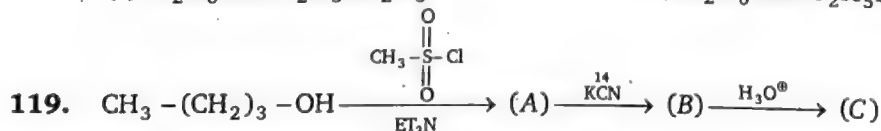
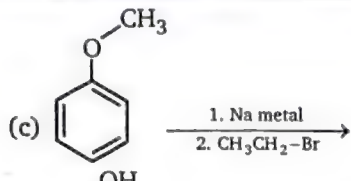
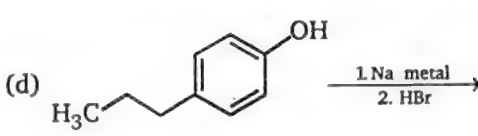
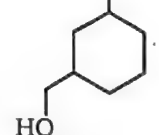
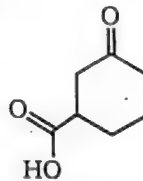
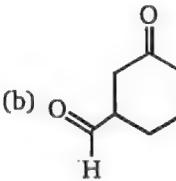
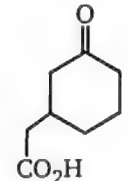
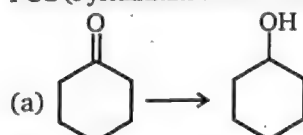
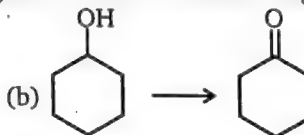
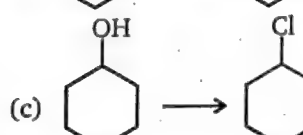
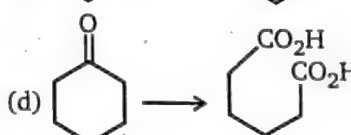
(a) $(A) = \begin{matrix} CH_2-OH \\ | \\ CH_2-SH \end{matrix}$ (b) $(B) = NaBH_4$ (c) $(C) = KMnO_4$ (d) $(D) = H_3O^{\oplus}$

117. In the Libermann's nitroso reaction, sequential changes in the colour of phenol occurs as :

(a) Brown or red ⟶ green ⟶ deep blue (b) Red ⟶ deep blue ⟶ green
(c) Red ⟶ green ⟶ white (d) White ⟶ red ⟶ green

118. Ethanol when reacts with PCl_5 gives A, $POCl_3$ and HCl. A reacts with dry Ag_2O to form B(major product) and AgCl. A and B respectively are :

(a) C_2H_5Cl and $C_2H_5OC_2H_5$ (b) C_2H_4 and $C_2H_5OC_2H_5$
(c) C_2H_6 and $C_2H_5OC_2H_5$ (d) C_2H_6 and $C_2H_5NO_2$

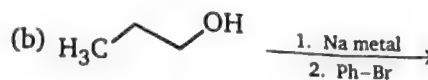
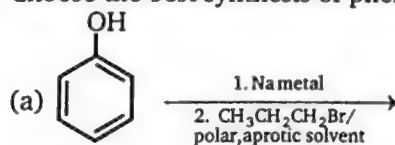
119. $CH_3-(CH_2)_3-OH \xrightarrow[ET_3N]{CH_3-SO_2-Cl} (A) \xrightarrow{K^{14}CN} (B) \xrightarrow{H_3O^{\oplus}} (C)$

Product (C) is :

(a) $CH_3-(CH_2)_3-CO_2H$ (b) $CH_3-(CH_2)_3-{}^{14}CO_2H$

(c) CH_3-CO_2H (d) $CH_3-\overset{O}{\overset{\|}{\underset{14}{C}}}-O-H$

120. Choose the best synthesis of phenyl n-propyl ether.

(a) Phenol (OH on benzene) $\xrightarrow[\text{2. } CH_3CH_2CH_2Br/\text{ polar, aprotic solvent}]{\text{1. Na metal}}$ (b) $H_3C\!\diagup\!\!\diagdown\!OH$ (propanol) $\xrightarrow[\text{2. Ph-Br}]{\text{1. Na metal}}$

(c) CH_3 O (methoxybenzene) $\xrightarrow[\text{2. } CH_3CH_2-Br]{\text{1. Na metal}}$ (d) H_3C ... OH (4-propylphenol) $\xrightarrow[\text{2. HBr}]{\text{1. Na metal}}$

121. OH, HO (3-(hydroxymethyl)cyclohexanol) $\xrightarrow{Na_2Cr_2O_7/H_2SO_4}$ The product obtained is :

(d) None of these

122. What is true for the equilibrium reaction ?

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + CH_3-OH \overset{\text{cat.}}{\rightleftharpoons} CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3 + H_2O$$

(a) The use of equimolar quantities of CH_3OH and CH_3COOH will give the greatest yield of the ester at equilibrium

(b) Removal of water will increase the amount of ester at equilibrium

(c) Addition of CH_3COOCH_3 will cause the formation of equal an equal number of moles of water

(d) Application of pressure increases the amount of ester at equilibrium

123. PCC (Pyridinium chloro chromate) is a good reagent for which of the following transformations ?

124. How many primary alcohols (including stereoisomers) are possible with formula $C_5H_{12}O$?

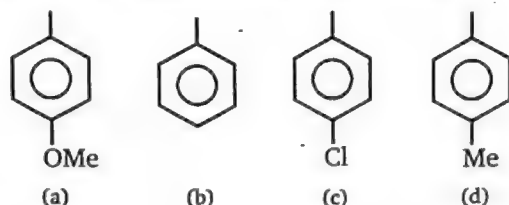
(a) Two (b) Three
(c) Four (d) Five

125. 1-Phenylethanol can be prepared by the reaction of benzaldehyde with the product obtained in the reaction between:

(a) CH_3I and Mg (b) C_2H_5I and Mg
(c) CH_3Br and $AlCl_3$ (d) CH_3OH and $ZnCl_2$

126. 0.092 g of a compound with the molecular formula $C_3H_8O_3$ on reaction with an excess of CH_3MgI gives 67.00 mL of methane at STP. The number of active hydrogen atoms present in a molecule of the compound is :

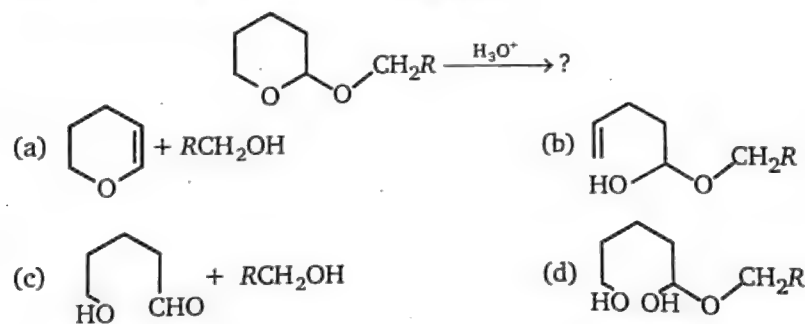
(a) one (b) two
(c) three (d) four

127. Migratory aptitude of the following in decreasing order is :

(a) a > c > b > d (b) a > d > b > c
(c) a > d > c > b (d) b > c > a > b

128. The major product formed in the reaction is :

$CH_2R \xrightarrow{H_3O^+} ?$

(a) + RCH_2OH (b) HO, O, CH_2R

(c) HO CHO + RCH_2OH (d) HO OH O CH_2R

129. Reaction of *R*-2-butanol with *p*-toluenesulphonyl chloride in pyridine then LiBr gives :

(a) *R*-2-butyl bromide (b) *S*-2-butyl tosylate
(c) *R*-2-butyl tosylate (d) *S*-2-butyl bromide

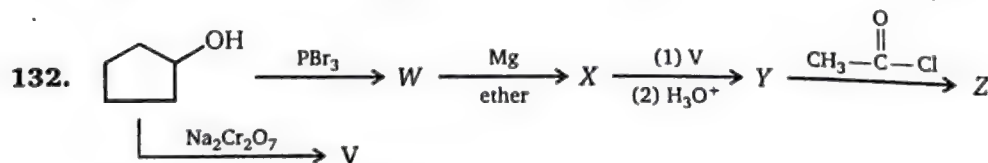
130. Optically active 2-octanol rapidly loses its optical activity when exposed to :

(a) dilute acid (b) dilute base (c) light (d) humidity

131. If (±) 2-methyl butanoic acid were esterified by reaction with (±) 2-butanol, how many optically active compounds would be present in the final equilibrium reaction mixture ?

(a) 2 (b) 3 (c) 4 (d) 6

132. (cyclopentyl)–OH $\xrightarrow{PBr_3} W \xrightarrow[\text{ether}]{Mg} X \xrightarrow[(2)\ H_3O^+]{(1)\ V} Y \xrightarrow{CH_3-\overset{O}{\overset{\|}{C}}-Cl} Z$

$\xrightarrow{Na_2Cr_2O_7} V$

Product *Z* of above reaction is :

(a) $O-\overset{O}{\overset{\|}{C}}-CH_3$ (attached at ring junction carbon of second cyclopentane, adjacent)

(b) $O-\overset{O}{\overset{\|}{C}}-CH_3$ (attached at the ring-junction carbon)

(c) $O-\overset{O}{\overset{\|}{C}}-CH_3$

(d) $O-\overset{O}{\overset{\|}{C}}-CH_3$

133. $Ph-CH(OH)-Ph \xrightarrow[AlCl_3]{LiAlH_4} (A)$; Identify the product :

(a) No reaction

(b) Ph–Ph

(c) $Ph-CH_2-Ph$

(d) $Ph-\overset{O}{\overset{\|}{C}}-Ph$

134. $(EtO)_2CHCHO + CH_3MgI \xrightarrow{H_3O^{\oplus}} (A)$

Product obtained in the above reaction is :

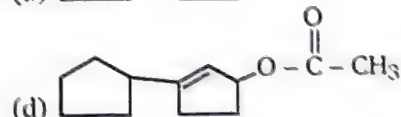
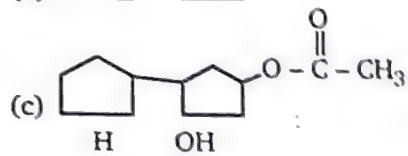
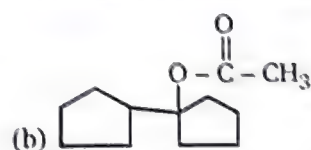
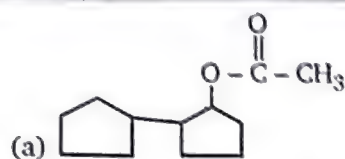
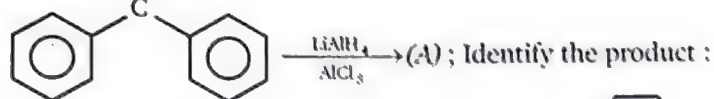
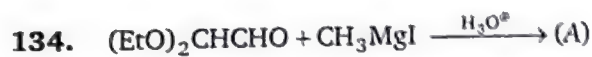
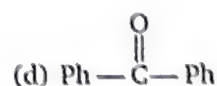
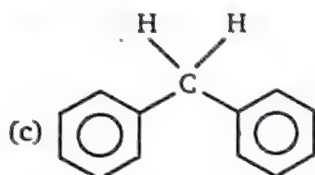
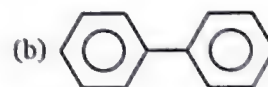
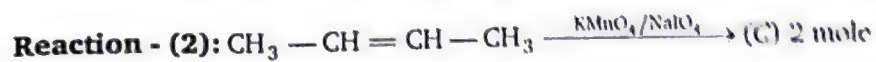
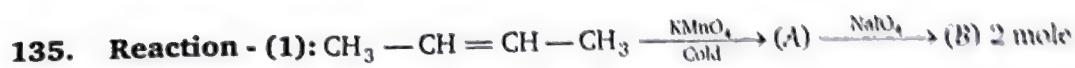
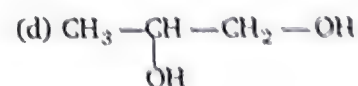
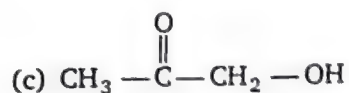
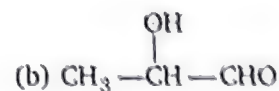
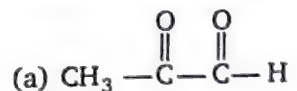
(a) $CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$

(b) $CH_3-\overset{OH}{\overset{|}{C}H}-CHO$

(c) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-OH$

(d) $CH_3-\underset{OH}{\underset{|}{C}H}-CH_2-OH$

135. **Reaction - (1):** $CH_3-CH=CH-CH_3 \xrightarrow[Cold]{KMnO_4} (A) \xrightarrow{NaIO_4} (B)$ 2 mole

Reaction - (2): $CH_3-CH=CH-CH_3 \xrightarrow{KMnO_4/NaIO_4} (C)$ 2 mole

Product (*B*) and (*C*) respectively are :

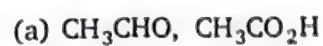
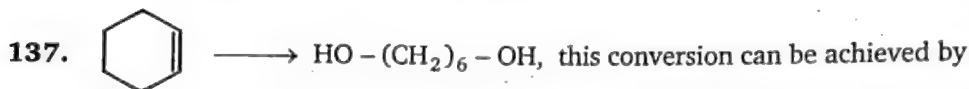
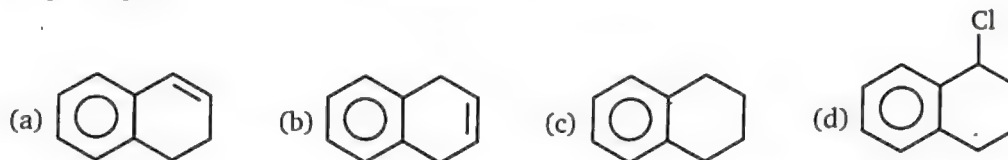
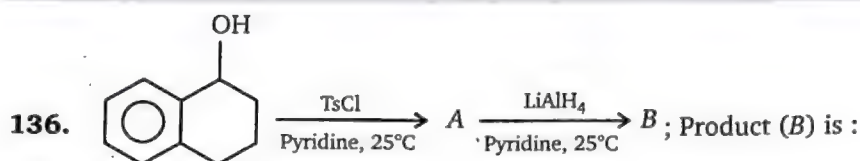
(a) CH_3CHO, CH_3CO_2H

(b) CH_3CO_2H, CH_3CHO

(c) CH_3CHO in both reaction

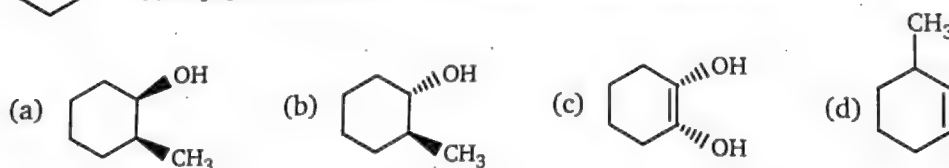
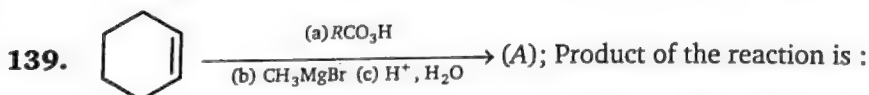
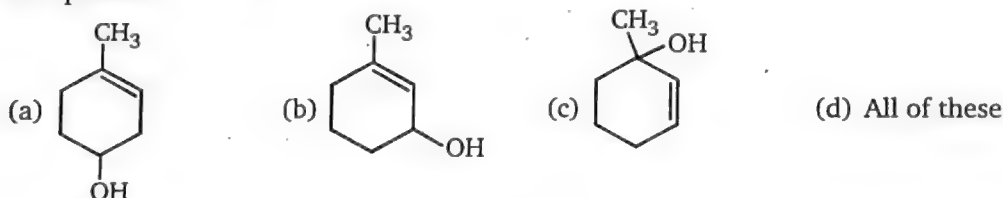
(d) CH_3CO_2H in both reaction

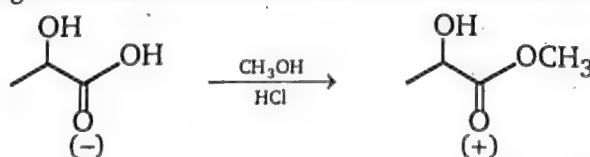
136. (Tetralin-1-ol, with OH) $\xrightarrow[\text{Pyridine, 25°C}]{\text{TsCl}}$ A $\xrightarrow[\text{Pyridine, 25°C}]{\text{LiAlH}_4}$ B ; Product (B) is :

137. (Cyclohexene) $\longrightarrow$ $HO-(CH_2)_6-OH$, this conversion can be achieved by

(a) O_3, Zn, then $LiAlH_4$ (b) O_3/H_2O_2, then $LiAlH_4$

(c) cold dil. $KMnO_4, HIO_4$, then $LiAlH_4$ (d) All of these

138. Which of the following alcohol on treatment with HCl give 3-chloro-3-methyl cyclohexene as a product ?

139. (Cyclohexene) $\xrightarrow[\text{(b) } CH_3MgBr \text{ (c) } H^+, H_2O]{\text{(a) } RCO_3H}$ (A); Product of the reaction is :

140. Esterification (shown below) is a reaction converting a carboxylic acid to its ester. It involves only the carbonyl carbon. Esterification of (–) -lactic acid with methanol yields (+)-methyl lactate. Assuming that there are no side reactions, what is true about this reaction ?

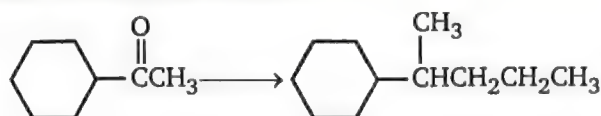
$CH_3CH(OH)COOH$ (–) $\xrightarrow[\text{HCl}]{CH_3OH}$ $CH_3CH(OH)COOCH_3$ (+)

(a) An S_{N^2} process has occurred, inverting the absolute configuration of the chiral center

(b) An S_{N^1} reaction at the chiral center has inverted the optical rotation

(c) A diastereomer has been produced; diastereomers have different physical properties including optical rotation

(d) Optical rotation is not directly related to absolute configuration, so the change in sign of rotation is merely a coincidence

141. Which of the following sets of reagents, used in the order shown, would successfully accomplish the conversion shown ?

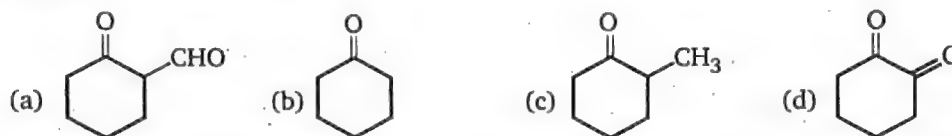
$$C_6H_{11}-\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow C_6H_{11}-\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_3$$

(a) $CH_3CH_2CH_2MgBr$; H_3O^+; PCC, CH_2Cl_2

(b) $CH_3CH_2CH_2MgBr$; H_3O^+; H_2SO_4, heat PCC, CH_2Cl_2

(c) $(C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCH_2CH_3, B_2H_6$; CH_3CO_2H

(d) $(C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCH_2CH_3$; H_2O

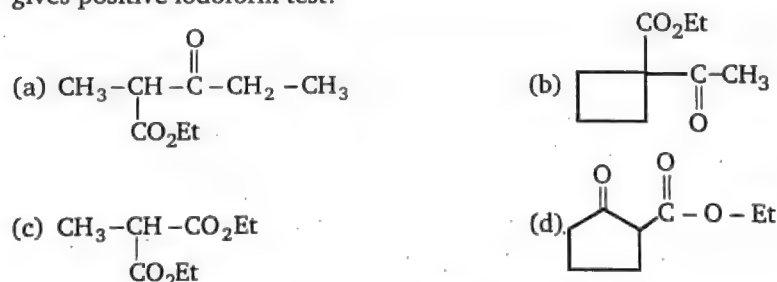
142. (2-oxocyclohexyl)CO_2Et $\xrightarrow[(2)\,\Delta]{(1)\ H_3O^+}$ Product ; Product of the reaction is :

(a) 2-oxocyclohexyl–CHO (b) cyclohexanone (c) 2-methylcyclohexanone (CH_3) (d) cyclohexane-1,2-dione (O, O)

143. Which of the following compound on hydrolysis followed by heating gives a product, which gives positive iodoform test?

(a) $CH_3-\underset{CO_2Et}{\underset{|}{C}H}-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

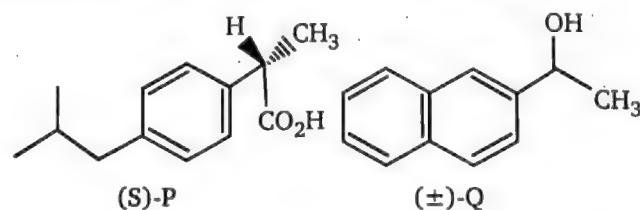
(b) cyclobutane bearing CO_2Et and $-\underset{O}{\underset{\|}{C}}-CH_3$ on the same carbon

(c) $CH_3-\underset{CO_2Et}{\underset{|}{C}H}-CO_2Et$

(d) 2-oxocyclopentyl$-\overset{O}{\overset{\|}{C}}-O-Et$

144. Treatment of a 2° OH with CrO_3/H_2SO_4 yields an/a :

(a) aldehyde (b) carboxylic acid (c) ester (d) ketone

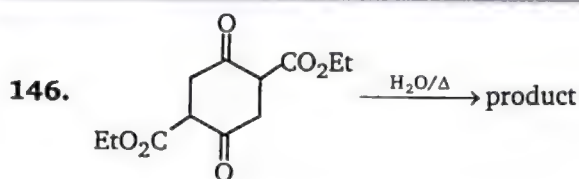
145. Esterification of the acid **P** with the alcohols **Q** will give :

(S)-P (±)-Q

(a) only one enantiomer

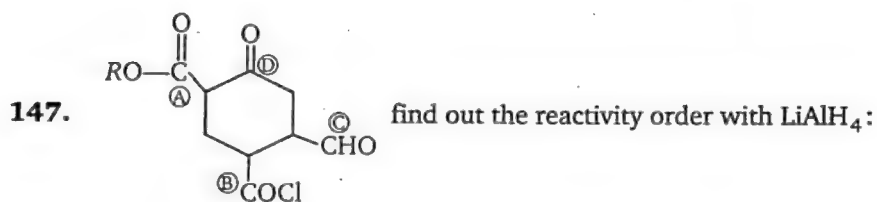
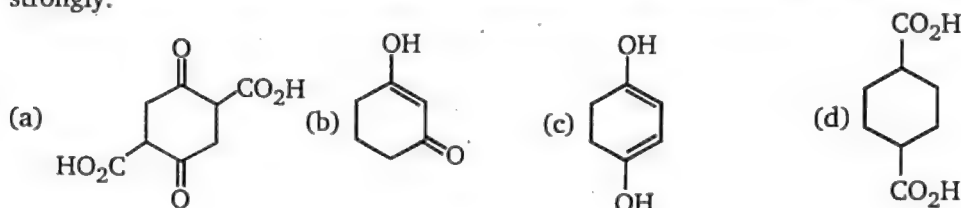
(b) a mixture of diastereomers

(c) a mixture of enantiomers

(d) only one diastereomer

146. [Structure: cyclohexane-1,4-dione with CO_2Et groups at C-2 and C-5 (diethyl succinylsuccinate)] $\xrightarrow{H_2O/\Delta}$ product

Identify major product of the reaction, when the given compound is hydrolysed and heated strongly:

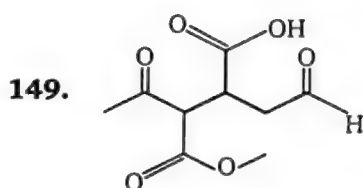
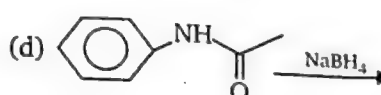
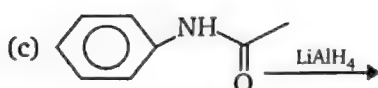
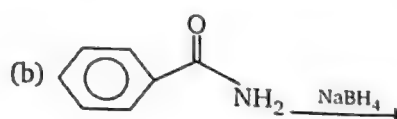
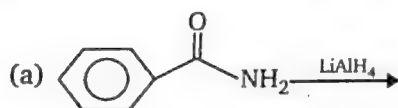
(a) [2,5-dioxocyclohexane-1,4-dicarboxylic acid: HO_2C, CO_2H] (b) [3-hydroxycyclohex-2-enone: OH, O] (c) [hydroquinone: OH, OH] (d) [cyclohexane-1,4-dicarboxylic acid: CO_2H, CO_2H]

147. [Structure: cyclohexane ring bearing RO–C(=O)– (Ⓐ), ring C=O (Ⓓ), CHO (Ⓒ), COCl (Ⓑ)] find out the reactivity order with $LiAlH_4$:

(a) $A > B > C > D$ (b) $B > C > D > A$
(c) $D > C > B > A$ (d) $B > D > C > A$

148. Find out the reaction in which obtained product give positive isocyanide test:

(a) $C_6H_5CONH_2 \xrightarrow{LiAlH_4}$ (b) $C_6H_5CONH_2 \xrightarrow{NaBH_4}$

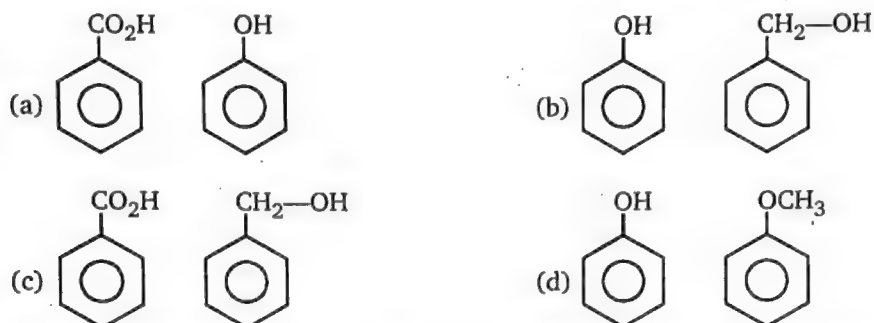
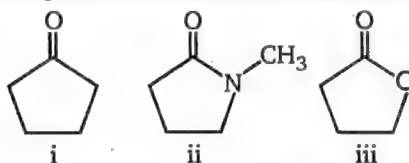
(c) $C_6H_5NHCOCH_3 \xrightarrow{LiAlH_4}$ (d) $C_6H_5NHCOCH_3 \xrightarrow{NaBH_4}$

149. [Structure: compound containing a ketone ($CH_3C=O$), a carboxylic acid (COOH), an aldehyde (CHO) and a methyl ester (CO_2CH_3)]

In the above given compound how many functional group reduced by LAH (Lithium aluminium hydride) and SBH (sodium borohydride) respectively ?

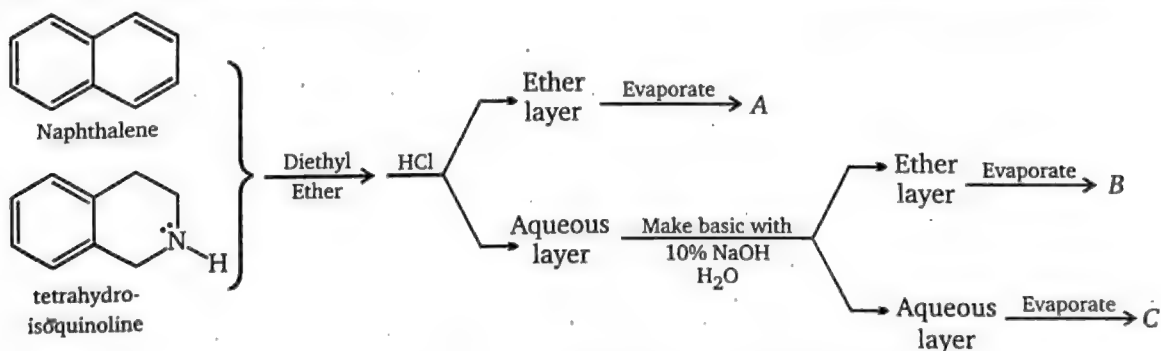
(a) 4, 4 (b) 4, 3 (c) 3, 4 (d) 4, 2

150. An unknown compound (A) (molarmass = 180) on acylation gives a product (molar mass = 390) than find the number of hydroxyl group present in compound (A).

(a) 5 (b) 6 (c) 10 (d) 1

151. Which of the following compound is differentiated by $NaHCO_3$ as well as by NaOH ?

152. Arrange the following compounds in order of their reactivity toward $LiAlH_4$.

(a) i < ii < iii (b) i < iii < ii

(c) ii < i < iii (d) ii < iii < i

153. Choose the statement that is true about *A*, *B* and *C* in the following separation scheme.

(a) *A* = tetrahydroisoquinoline, *B* = naphthalene and *C* = inorganic ions such as Na^+ and Cl^-

(b) *A* = naphthalene, *B* = tetrahydroisoquinoline and *C* = inorganic ions such as Na^+ and Cl^-

(c) *A* = inorganic ions such as Na^+ and Cl^-, *B* = naphthalene and *C* = tetrahydroisoquinoline

(d) *A* = inorganic ions such as Na^+ and Cl^-, *B* = naphthalene and *C* = tetrahydroisoquinoline

154. (Structure: naphthalene bearing O-(p-methoxyphenyl), OH, $CH_2—OH$ and $CH=CH_2$ groups; $O—CH_3$, CH_2) $\xrightarrow{xHI}$ value of x is :

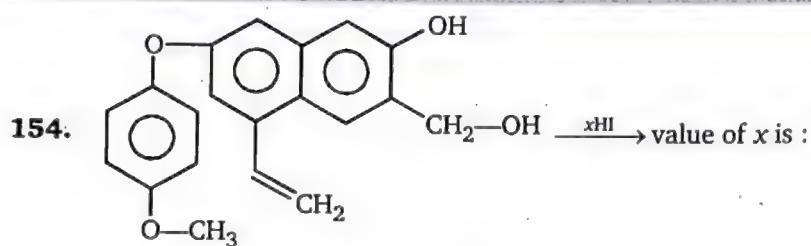
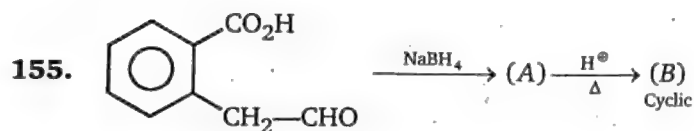
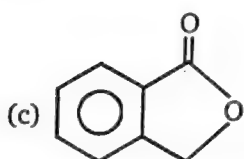
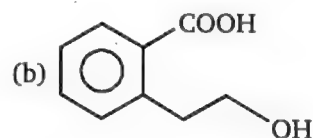
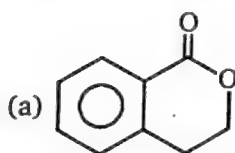
(a) 2 (b) 3 (c) 4 (d) 5

155. (Benzene ring with CO_2H and $CH_2—CHO$) $\xrightarrow{NaBH_4}$ (A) $\xrightarrow[\Delta]{H^{\oplus}}$ (B) Cyclic

Compound (B) is :

(a) (bicyclic lactone: O, O)

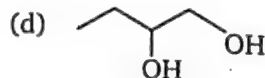
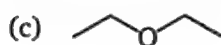
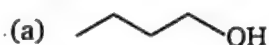
(b) (benzene ring with COOH and CH_2CH_2OH) COOH, OH

(c) (five-membered lactone: O, O)

(d) (a) and (c) both

156. 1-Phenoxypropane is treated with excess of conc. HI at 0°C and the mixture of products is treated with thionyl chloride. The products formed are

(a) n-propanol + Chlorobenzene
(b) Phenol + n-propyl iodide
(c) n-propyl chloride + Chlorobenzene
(d) n-propyl chloride + Phenol

157. Amongst the following compounds, the compound having the lowest boiling point is

(a) (butan-1-ol skeletal) OH
(b) (pentan-1-ol skeletal) OH
(c) (diethyl ether skeletal) O
(d) (butane-1,2-diol skeletal) OH, OH

ANSWERS — LEVEL 1															
1.	(c)	**2.**	(a)	**3.**	(b)	**4.**	(c)	**5.**	(b)	**6.**	(b)	**7.**	(b)	**8.**	(a)
9.	(b)	**10.**	(b)	**11.**	(b)	**12.**	(b)	**13.**	(a)	**14.**	(a)	**15.**	(a)	**16.**	(a)
17.	(d)	**18.**	(a)	**19.**	(b)	**20.**	(a)	**21.**	(a)	**22.**	(a)	**23.**	(d)	**24.**	(a)
25.	(b)	**26.**	(b)	**27.**	(b)	**28.**	(b)	**29.**	(c)	**30.**	(c)	**31.**	(b)	**32.**	(b)
33.	(a)	**34.**	(b)	**35.**	(b)	**36.**	(c)	**37.**	(c)	**38.**	(c)	**39.**	(d)	**40.**	(c)
41.	(b)	**42.**	(b)	**43.**	(d)	**44.**	(d)	**45.**	(b)	**46.**	(a)	**47.**	(b)	**48.**	(b)
49.	(a)	**50.**	(b)	**51.**	(a)	**52.**	(c)	**53.**	(c)	**54.**	(c)	**55.**	(b)	**56.**	(a)
57.	(d)	**58.**	(c)	**59.**	A-d	**59.**	B-b	**59.**	C-a	**60.**	(c)	**61.**	(c)	**62.**	A-b
62.	B-b	**63.**	(b)	**64.**	(c)	**65.**	(b)	**66.**	(a)	**67.**	(a)	**68.**	(d)	**69.**	(a)
70.	(c)	**71.**	(b)	**72.**	(d)	**73.**	(d)	**74.**	(c)	**75.**	(b)	**76.**	(d)	**77.**	(c)
78.	(c)	**79.**	(d)	**80.**	(c)	**81.**	(c)	**82.**	(d)	**83.**	(a)	**84.**	(b)	**85.**	(b)
86.	(c)	**87.**	(c)	**88.**	(b)	**89.**	(d)	**90.**	(a)	**91.**	(c)	**92.**	(b)	**93.**	(b)
94.	(a)	**95.**	(d)	**96.**	(b)	**97.**	(c)	**98.**	(a)	**99.**	(c)	**100.**	(a)	**101.**	(d)
102.	(b)	**103.**	(c)	**104.**	(c)	**105.**	(d)	**106.**	(c)	**107.**	(b)	**108.**	(a)	**109.**	(c)
110.	(d)	**111.**	(c)	**112.**	(b)	**113.**	(b)	**114.**	(b)	**115.**	(b)	**116.**	(d)	**117.**	(b)
118.	(a)	**119.**	(b)	**120.**	(a)	**121.**	(a)	**122.**	(b)	**123.**	(b)	**124.**	(d)	**125.**	(a)
126.	(c)	**127.**	(b)	**128.**	(c)	**129.**	(d)	**130.**	(a)	**131.**	(c)	**132.**	(b)	**133.**	(c)
134.	(b)	**135.**	(a)	**136.**	(c)	**137.**	(d)	**138.**	(d)	**139.**	(b)	**140.**	(d)	**141.**	(c)
142.	(b)	**143.**	(b)	**144.**	(d)	**145.**	(b)	**146.**	(c)	**147.**	(b)	**148.**	(a)	**149.**	(d)
150.	(a)	**151.**	(c)	**152.**	(d)	**153.**	(b)	**154.**	(b)	**155.**	(a)	**156.**	(b)	**157.**	(c)

LEVEL-2

1. Consider the pairs of ethers, numbered I through V, shown below. To the right of each pair is a description of reaction conditions to be applied to each. One compound of the pair will react more rapidly than the other.

Which ether of the two will be more rapidly cleaved?

Write your answer in box.

	(A) Ether Pairs	(B)	Cleavage Conditions
I.	C_6H_5–O—$CH(CH_3)_2$ &	(H_3C, H_3C)C_6H_3–O—CH_3	Treated with HBr in CH_3CN, 40°C
II.	(H_3C, H_3C)C_6H_{10}–O—$C(CH_3)_3$ &	(C_2H_5, C_2H_5)C_6H_{10}–O—CH_3	Treated with H_2SO_4 in CH_3CN, 40°C
III.	C_6H_5–O–(structure) &	C_6H_5–O–(structure)	Treated with H_2SO_4 in CH_3CN, 40°C
IV.	CH_3O–(ring O)–OH &	OH–(ring O)–OCH_3	Treated with 5% aqueous H_2SO_4, 25°C
V.	(structure)–O–$CH(CH_3)_2$ &	(structure)–O–$CH(CH_3)_2$	Treated with 5% aqueous H_2SO_4, 25°C

2. Comprehension

(a) $CH_3-CH_2-CH_2-CH_2-CH_2-OH$

(b) $CH_3-CH_2-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

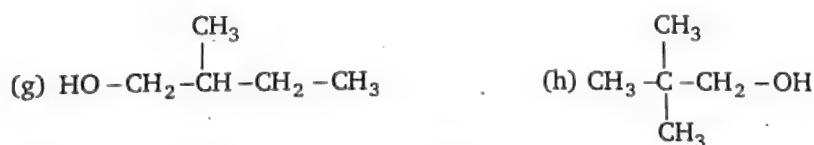
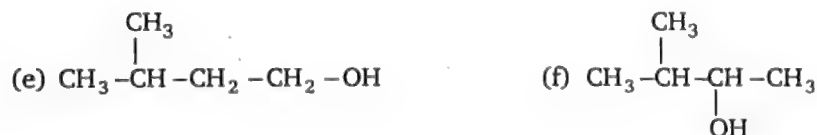
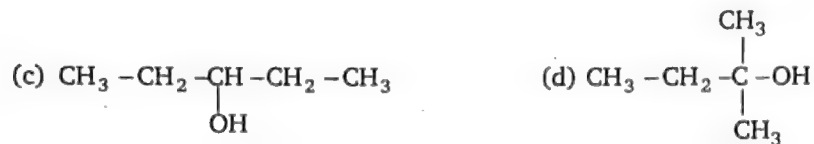
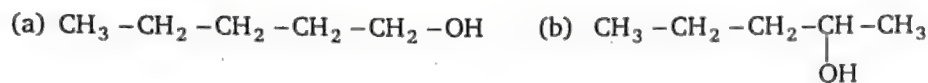
(c) $CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_3$

(d) $CH_3-CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH$

(e) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-CH_2-OH$

(f) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

(g) $HO-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-CH_3$

(h) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2-OH$

Above compounds (a) to (h) are isomers of $C_5H_{12}O$.

Based on the above isomer answer the following (A to F).

A. Which isomer is most reactive towards dehydration by conc. H_2SO_4?

B. Which isomer will undergo rearrangement when treated with conc. H_2SO_4?

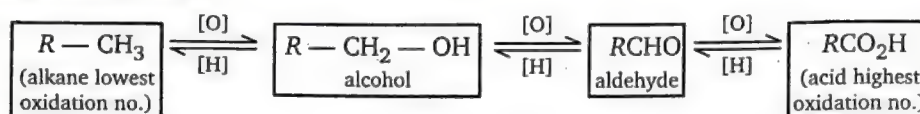
C. Which isomers on dehydration with conc. H_2SO_4 give alkene which is capable to show geometrical isomerism ?

D. Which isomer is least acidic ?

E. Which isomers on dehydration give most stable alkene ?

F. Which isomer on dehydration with conc. H_3PO_4 undergo maximum rearrangement ?

3. Comprehension

$R-CH_3$ (alkane lowest oxidation no.)	$\underset{[H]}{\overset{[O]}{\rightleftharpoons}}$	$R-CH_2-OH$ alcohol	$\underset{[H]}{\overset{[O]}{\rightleftharpoons}}$	$RCHO$ aldehyde	$\underset{[H]}{\overset{[O]}{\rightleftharpoons}}$	RCO_2H (acid highest oxidation no.)

[O] = Oxidation [H] = Reduction

Consider the above sequence and answer *A* to *F*.

A. Conversion $(CH_3-CH_3 \longrightarrow CH_3-CH_2-OH)$ alkane $\longrightarrow$ alcohol is achieved by:

(a) Br_2/hv, alc. KOH (b) Br_2/hv, aq. KOH
(c) Br_2/CCl_4, $LiAlH_4$ (d) Br_2/CCl_4, $NaBH_4$

B. Conversion $R-CH_2-OH \longrightarrow R-CHO$ can be done by:

(a) PCC/CH_2Cl_2 (b) Cu, 300°C
(c) CrO_3 (d) All of these

C. Conversion $R-CHO \longrightarrow R-CO_2H$ can be done by:

(a) $KMnO_4$ (b) H_2CrO_4
(c) $K_2Cr_2O_7$ (d) All of these

D. Conversion $R-CO_2H \longrightarrow R-CHO$ can be done by:

(a) $LiAlH_4$ (b) $NaBH_4$
(c) DIBAL – H (d) All of these

E. Conversion $R-CHO \longrightarrow R-CH_2-OH$ can be done by:

(a) $LiAlH_4$ (b) $NaBH_4$
(c) H_2/Ni (d) All of these

F. Reduction $R-CH_2-OH \longrightarrow R-CH_3$ can be done by:

(a) $LiAlH_4$ (b) $NaBH_4-AlCl_3$
(c) H_2-Ni (d) Red P + HI

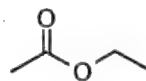
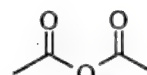
4. Which of the following is true for 3-methylbutanal ?

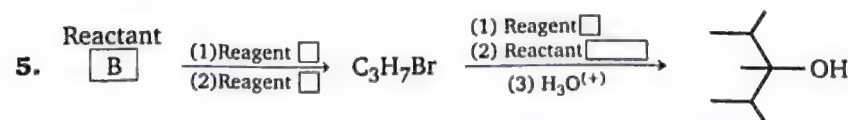
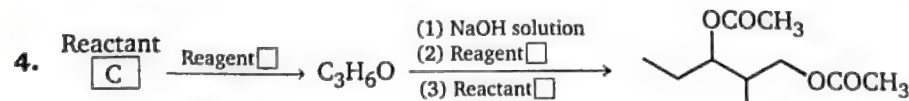
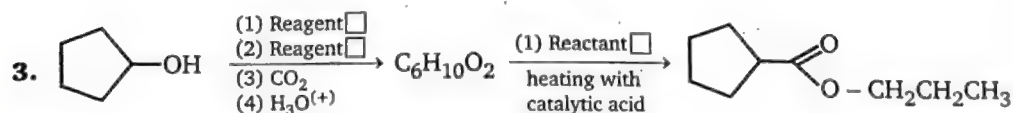
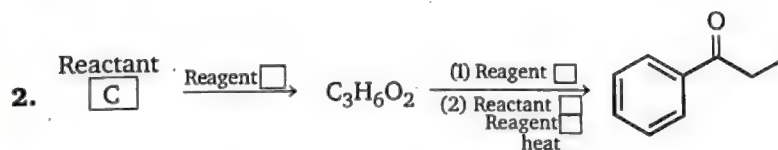
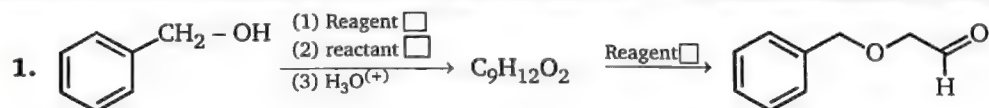
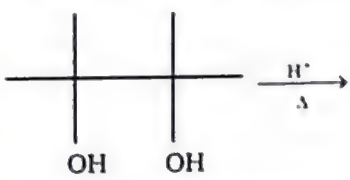
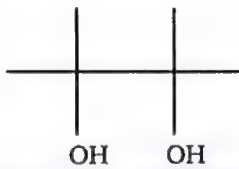
a.	This compound may be classified as an aldehyde.	
b.	This compound may be classified as a ketone	
c.	An aldol reaction takes place on treatment with NaOH solution.	
d.	There is no reaction with $LiAlH_4$ in ether solution.	
e.	An excess of CH_3MgBr in ether reacts to give 4-methyl-2-pentanol.	
f.	Wolff-Kishner reduction gives butane.	
g.	This compound is an isomer of 3-pentanone.	

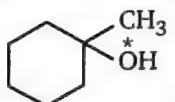
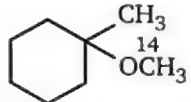
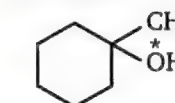
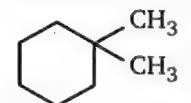
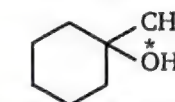
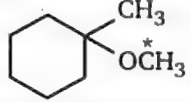
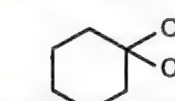
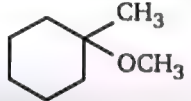
5. This problem is an introduction to the planning of multistep syntheses.

For use, you have six reactant compounds (**A** through **F**) ; and eight reagents (**1** through **8**), shown below.

Following these lists, five multistep syntheses are outlined. For each of these, certain reactants or reagents must be identified by writing an appropriate letter or number in designated answer boxes. Write a single letter or number, indicating your choice of the best reactant or reagent, in each answer box.

Reactant Compounds :

Reagents :

(1) Jones' reagent [$Na_2Cr_2O_7$ in H_3O^+]
(2) PCC [CrO_3 in pyridine + HCl]
(3) Sodium hydride NaH
(4) Sodium borohydride $NaBH_4$
(5) Thionyl chloride $SOCl_2$
(6) Phosphorus tribromide PBr_3
(7) Aluminium trichloride $AlCl_3$
(8) Magnesium turnings in ether

6. Which of the following is true for 3-methyl-2-butanone?

a.	It may be prepared by CrO_3 oxidation of 2-methyl-2-butanol.	
b.	Its reaction with $NaBH_4$ gives a secondary alcohol.	
c.	It may be prepared by acidic Hg^{2+} catalyzed hydration of 3-methyl-1-butyne.	
d.	It forms a silver mirror on treatment with $[Ag(NH_3)_2]^+$.	
e.	This compound is an isomer of 4-penten-1-ol.	

7. Which of these methods would serve to prepare 1-phenyl-2-propanol?

a.	Addition of benzyl Grignard reagent to acetaldehyde (ethanal).	
b.	Addition of phenyl lithium to propylene oxide (methyloxirane).	
c.	Addition of phenyl Grignard reagent to acetone (2-propanone).	
d.	Acid-catalyzed hydration (addition of water to) of 2-phenyl-1-propene.	
e.	Addition of methyl Grignard reagent to acetophenone (methyl phenyl ketone).	
f.	Addition of methyl Grignard reagent to phenylacetaldehyde.	

8. Match the Column (I) and (II).

Column (I)		Column (II)	
Reaction		**Name of Reaction**	
(a)	(pinacol skeleton with two OH groups: OH OH) $\xrightarrow[\Delta]{H^+}$	**(p)**	Pinacol-Pinacolone rearrangement

(b)	2-amino-alcohol (OH, NH_2) $\xrightarrow[2HCl]{NaNO_2}$	(q)	Semi-Pinacol reaction
(c)	tetramethyl epoxide (O) $\xrightarrow[\Delta]{H^+}$	(r)	Pinacolic-Diazotization
(d)	pinacol (OH, OH) $\xrightarrow[(2)\ Et_3N, \Delta]{(1)\ TsCl,}$	(s)	Pinacol fashion reaction

9. **Match the Column (I) and (II).**

Column (I)		Column (II)	
Reactant		**Products**	
(a)	1-methylcyclohexanol (CH_3, $\overset{*}{O}H$) $\xrightarrow[H_2SO_4\ Conc.]{CH_3OH}$	(p)	1-methylcyclohexyl (CH_3, $^{14}OCH_3$)
(b)	1-methylcyclohexanol (CH_3, $\overset{*}{O}H$) $\xrightarrow[(2)\ CH_3I]{(1)\ NaH}$	(q)	1,1-dimethylcyclohexane (CH_3, CH_3)
(c)	1-methylcyclohexanol (CH_3, $\overset{*}{O}H$) $\xrightarrow[(2)\ Mg\ (3)\ CH_3I]{(1)\ HBr}$	(r)	1-methylcyclohexyl (CH_3, $\overset{*}{O}CH_3$)
(d)	1-methylcyclohexanol (CH_3, OH) $\xrightarrow[(2)\ {}^{14}CH_3I]{(1)\ Na}$	(s)	1-methylcyclohexyl (CH_3, OCH_3)

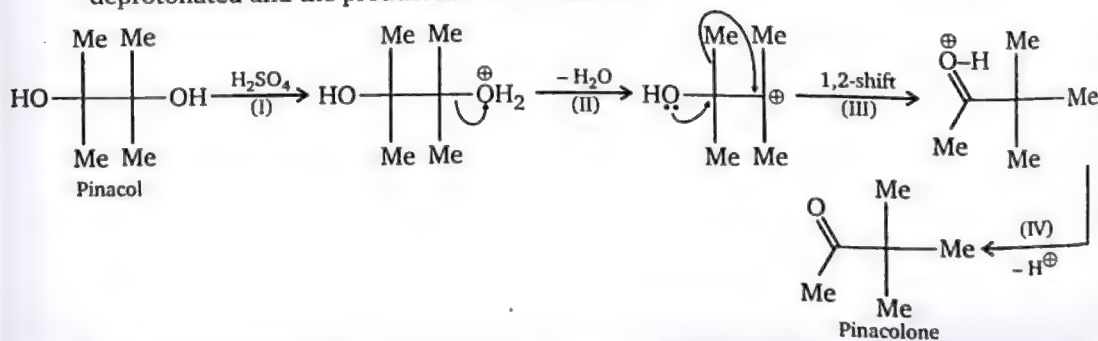
10.

Reaction 1.	Fischer projection: CH_2-OH / $C=O$ / HO–C–H / H–C–OH / H–C–OH / CH_2OH $\xrightarrow{5HIO_4}$
Reaction 2.	Fischer projection: CHO / HO–C–H / H–C–OH / H–C–OH / H–C–OH / CH_2OH $\xrightarrow{5HIO_4}$

Ratio of moles of formaldehyde obtained in the reaction (1) and reaction (2) ?

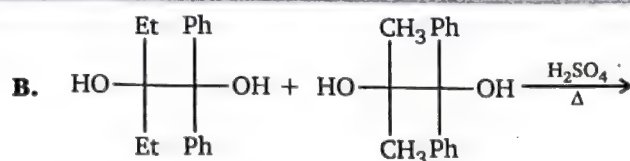
11. Comprehension

Di-tert-glycols rearrange in the presence of acid to give α-tertiary ketones. The trivial name of the simplest glycol of this type is pinacol, and this type of reaction therefore is named pinacol rearrangement (in this specific case, the reaction is called a pinacol-pinacolone rearrangement). The rearrangement involves 4 steps. one of the hydroxyl groups is protonated in the first step. A molecule of water is eliminated in the second step and a tertiary carbocation is formed. The carbocation rearranges in the third step into a more stable carboxonium ion *via* a [1, 2] rearrangement. In the last step, the carboxonium ion is deprotonated and the product ketone is obtained.

Pinacol $\xrightarrow[(I)]{H_2SO_4}$ $HO-C(Me)_2-C(Me)_2-\overset{\oplus}{O}H_2$ $\xrightarrow[(II)]{-H_2O}$ $HO-C(Me)_2-\overset{\oplus}{C}(Me)_2$ $\xrightarrow[(III)]{1,2\text{-shift}}$ $Me-C(=\overset{\oplus}{O}-H)-C(Me)_3$ $\xrightarrow[-H^{\oplus}]{(IV)}$ $Me-C(=O)-C(Me)_3$ (Pinacolone)

A. What is R.D.S. of pinacol-pinacolone rearrangement ?

(a) I step (b) II step

(c) III step (d) IV step

B. HO–C(Et)(Et)–C(Ph)(Ph)–OH + HO–C(CH_3)(CH_3)–C(Ph)(Ph)–OH $\xrightarrow[\Delta]{H_2SO_4}$

How many products obtained in above reaction ?

(a) 1 (b) 2 (c) 3 (d) 4

C. 1-(chloromethyl)cyclopentan-1-ol ($-CH_2-Cl$, OH) $\xrightarrow[\Delta]{AgNO_3} P$

Product '*P*' is :

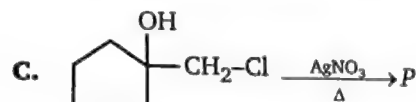
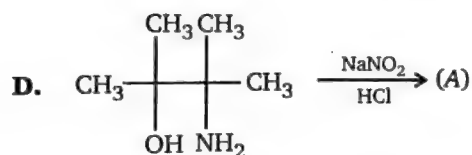
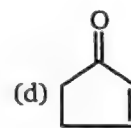
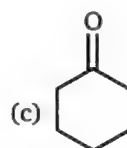
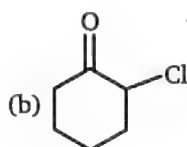
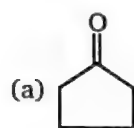
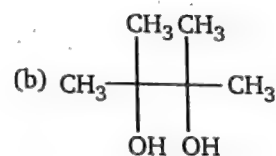
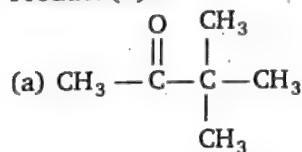
(a) cyclopentanone (b) 2-chlorocyclohexanone (c) cyclohexanone (d) cyclopentenone

D. CH_3–C(CH_3)(OH)–C(CH_3)(NH_2)–CH_3 $\xrightarrow[HCl]{NaNO_2}$ (*A*)

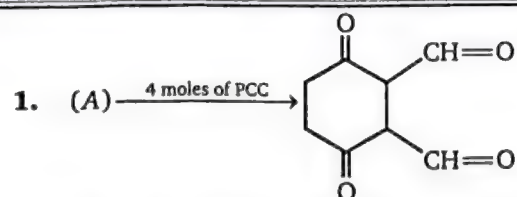
Product (*A*) is :

(a) $CH_3-\overset{O}{\overset{\|}{C}}-C(CH_3)_2-CH_3$

(b) CH_3–C(CH_3)(OH)–C(CH_3)(OH)–CH_3

(c) tetramethylethylene

(d) None of these

SUBJECTIVE PROBLEMS

1. (*A*) $\xrightarrow{\text{4 moles of PCC}}$ cyclohexane-1,4-dione with two $CH{=}O$ groups

Maximum number of moles of Ac_2O consumed by reactant (*A*) is :

ANSWERS — LEVEL 2

1. I – B; II – A; III – A; IV – B; V – B
2. A – d; B – a, c, e, f, g, h; C – a, b, c; D – d; E – d, e, f, g, h; F – e
3. A – b; B – d, C – d, D – c, E – d; F – d
4. a, c, e, g
5. Benzyl alcohol ($C_6H_5CH_2-OH$) $\xrightarrow[(3)\ H_3O^{(+)}]{(1)\ \text{Reagent [3]}\ (2)\ \text{reactant [d]}}$ $C_9H_{12}O_2$ $\xrightarrow{\text{Reagent [2]}}$ $C_6H_5CH_2-O-CH_2-CHO$

Reactant [C] $\xrightarrow{\text{Reagent [1]}}$ $C_3H_6O_2$ $\xrightarrow[(2)\ \text{Reactant [A]}\ \text{Reagent [7]}\ \text{heat}]{(1)\ \text{Reagent [5]}}$ + & $C_6H_5COCH_2CH_3$

Cyclopentanol (cyclopentyl–OH) $\xrightarrow[(3)\ CO_2\ (4)\ H_3O^{(+)}]{(1)\ \text{Reagent [6]}\ (2)\ \text{Reagent [8]}}$ $C_6H_{10}O_2$ $\xrightarrow[\text{heating with catalytic acid}]{(1)\ \text{Reactant [C]}}$ cyclopentyl–C(=O)–$O-CH_2CH_2CH_3$

Reactant [C] $\xrightarrow{\text{Reagent [2]}}$ C_3H_6O $\xrightarrow[(3)\ \text{Reactant [F]}]{(1)\ \text{NaOH solution}\ (2)\ \text{Reagent [4]}}$ $CH_3CH_2CH(OCOCH_3)CH(CH_3)CH_2OCOCH_3$

Reactant [B] $\xrightarrow[(2)\ \text{Reagent [6]}]{(1)\ \text{Reagent [4]}}$ C_3H_7Br $\xrightarrow[(3)\ H_3O^{(+)}]{(1)\ \text{Reagent [8]}\ (2)\ \text{Reactant [C or F]}}$ $((CH_3)_2CH)_2C(CH_3)-OH$

6. b, c, e
7. a, b, f
8. a – p, b – r, c – s, d – q
9. a – s, b – r, c – q, d – p
10. Ratio of reaction I and II = 2
11. A – b; B – b; C – c; D – a

Subjective Problems

1. 4

7 ALDEHYDES AND KETONES

LEVEL - 1

1. $\xrightarrow[\text{(Wolff-Kishner reduction)}]{N_2H_4/KOH/H_2O}$ $(A)_{\text{major}}$; Product A is :

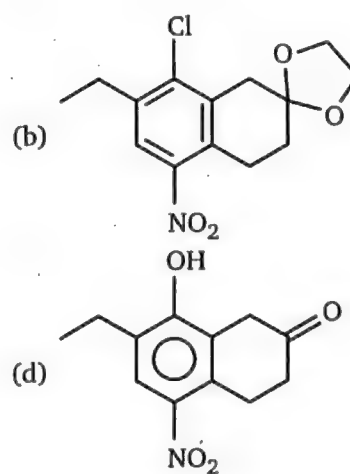
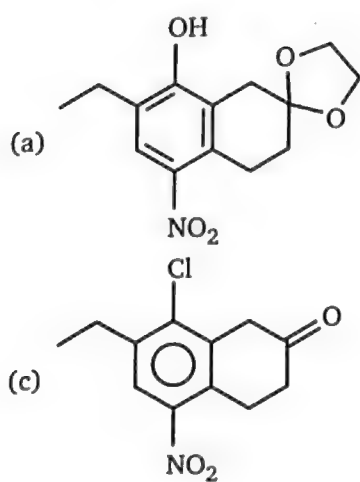
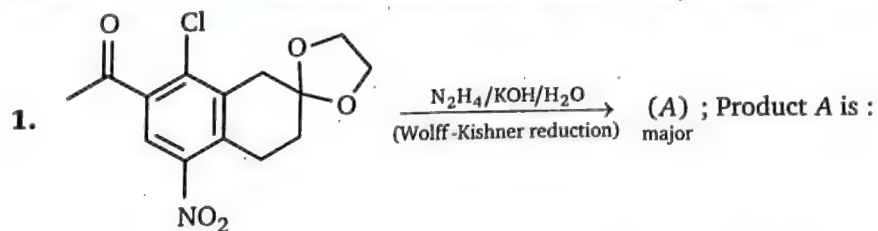
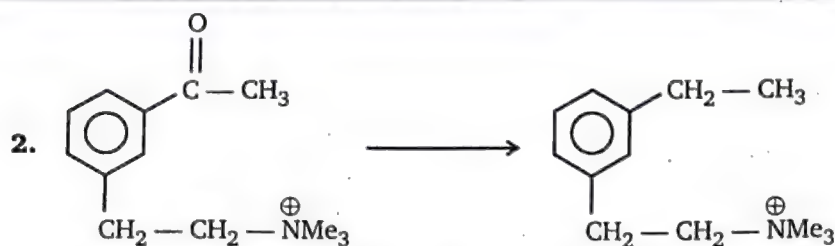
(a)

(b)

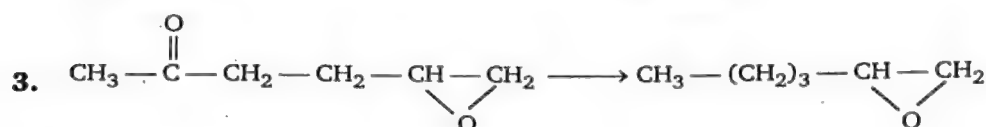
(c)

(d)

2. (3-acetylphenyl)–$CH_2-CH_2-\overset{\oplus}{N}Me_3$ $\longrightarrow$ (3-ethylphenyl)–$CH_2-CH_2-\overset{\oplus}{N}Me_3$

(Reactant: benzene ring bearing $\overset{O}{\overset{||}{C}}-CH_3$ and, meta to it, $CH_2-CH_2-\overset{\oplus}{N}Me_3$; product: benzene ring bearing CH_2-CH_3 and $CH_2-CH_2-\overset{\oplus}{N}Me_3$)

Above conversion can be achieved by :

(a) Wolf-Kishner reduction. (b) Clemmensen reduction
(c) $LiAlH_4$ (d) $NaBH_4$

3. $CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_2-\underset{\diagdown O \diagup}{CH-CH_2} \longrightarrow CH_3-(CH_2)_3-\underset{\diagdown O \diagup}{CH-CH_2}$

Above conversion can be achieved by :

(a) Wolff- Kishner reduction
(b) Clemmensen reduction
(c) $HS-CH_2-CH_2-SH$, following by Raney Ni
(d) None of these

4. (3-nitroacetophenone: benzene ring with $\overset{O}{\overset{||}{C}}-CH_3$ and NO_2 meta) $\xrightarrow[HCl]{Zn(Hg)}$; Product of the Clemmensen reduction is :

(a) benzene ring with CH_2-CH_3 and NO_2 (meta)
(b) benzene ring with $\overset{OH}{\overset{|}{CH}}-CH_3$ and NO_2 (meta)
(c) benzene ring with CH_2-CH_3 and NH_2 (meta)
(d) benzene ring with $\overset{OH}{\overset{|}{CH_2}}-CH_3$ and NO_2 (meta)

5. $CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-CH_2-\overset{O}{\overset{||}{C}}-CH_3 \longrightarrow CH_3-\overset{OH}{\overset{|}{CH}}-(CH_2)_3-CH_3$

Above conversion can be achieved by :

(a) Wolff-Kishner reduction (b) Clemmensen reduction
(c) $LiAlH_4$ (d) $NaBH_4$

6. [Reaction scheme: 4-(4-hydroxycyclohexyl)acetophenone (ring with $C(=O)-CH_3$ and OH) $\xrightarrow[HCl]{Zn(Hg)}$ (A); $\xrightarrow[HO^-/\Delta]{NH_2-NH_2}$ (B)]

Products: (P) CH_2-CH_3 substituted benzene attached to cyclohexane with OH; (Q) CH_2-CH_3 substituted benzene attached to cyclohexane with Cl; (R) CH_2-CH_3 substituted benzene attached to cyclohexene with Cl

Identify product (*A*) & (*B*) from the given product *P*, *Q*, *R*:

(a) $A = P, B = Q$ (b) $A = Q, B = R$ (c) $A = Q, B = P$ (d) $A = R, B = P$

7. [Structure: HO-cyclopentane with $C(=O)-CH_3$] $\xrightarrow[HCl]{Zn(Hg)}$ (*A*) ; Identify the *A*.

(a) [HO-cyclopentane with CH_2-CH_3] (b) [Cl-cyclopentane with ethyl]

(c) [Cl-cyclopentane with ethyl and methyl] (d) [cyclopentane with ethyl and OH]

8. [Structure: benzene with $C(=O)-CH_3$ and CH_2-CH_2-Br] $\xrightarrow[\text{(Wolff-Kishner reduction)}]{N_2H_4 \\ HO^-, \Delta}$ (*A*) ; Product (*A*) is :

(a) [benzene with CH_2-CH_3 and CH_2-CH_2-OH] (b) [benzene with ethyl and vinyl]

(c) $CH_3CH_2-C_6H_4-CH_2-CH_2-Br$ (para)

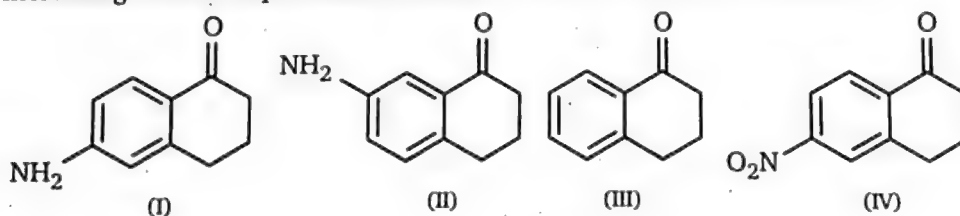
(d) $CH_3CH_2-C_6H_4-CH(Br)-CH_3$ (para)

9. [2-(2-oxopropyl)cyclohexanone ethylene ketal] $\xrightarrow{?}$ [2-propylcyclohexanone ethylene ketal] ;

Above conversion can be carried out by :

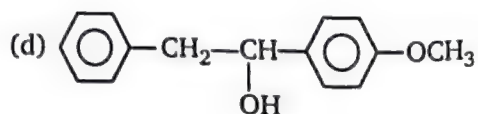
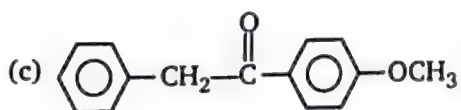
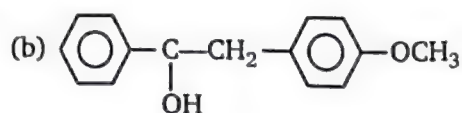
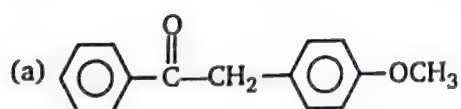
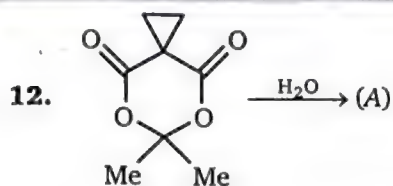
(a) Clemmensen reduction
(b) Wolff-Kishner reduction
(c) $LiAlH_4$
(d) $NaBH_4$

10. Increasing order of equilibrium constants for the formation of a hydrate:

(I) amino-substituted tetralone (NH_2)
(II) amino-substituted tetralone (NH_2)
(III) tetralone
(IV) nitro-substituted tetralone (O_2N)

(a) IV < III < II < I
(b) IV < III < I < II
(c) I < II < III < IV
(d) II <III < I < IV

11. $C_6H_5-C\equiv C-C_6H_4-OCH_3 \xrightarrow[\text{dil. } H_2SO_4]{HgSO_4}$ (A) Major product. Product (A) is:

(a) $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2-C_6H_4-OCH_3$
(b) $C_6H_5-\underset{OH}{\underset{|}{C}}-CH_2-C_6H_4-OCH_3$
(c) $C_6H_5-CH_2-\overset{O}{\overset{\|}{C}}-C_6H_4-OCH_3$
(d) $C_6H_5-CH_2-\underset{OH}{\underset{|}{CH}}-C_6H_4-OCH_3$

12. [Structure: 6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione] $\xrightarrow{H_2O}$ (A)

Predict the product of hydrolysis of the above molecule.

(a) [Structure: six-membered lactone with C(=O)–O–H and CH_3 substituents] (b) [Structure: cyclopentanone with CO_2H]

(c) [Structure: five-membered lactone with C(=O)–O–H] (d) [Structure: five-membered lactone with CO_2H]

13. [Structure: cyclohexane-1,2,4-triol] $\longrightarrow$ [Structure: 3,4-dihydroxycyclohexanone], This conversion can be achieved by :

(a) $Me_2CO/H^+, H_3O^{\oplus}, KMnO_4/HO^-$ (b) $Me_2CO/H^+, KMnO_4, H_3O^+$

(c) $KMnO_4/NaO_4$, Me_2CO/H^+, H_3O^+ (d) $KMnO_4/NaIO_4$, H_3O^+, Me_2CO/H^+

14. [Structure: vinyl ether] $\xrightarrow{H_3O^{\oplus}}$ *A* + *B*. Compound (*A*) & (*B*) can be differentiated by:

(a) 2-4-DNP (b) Fehling solution

(c) Lucas reagent (d) $NaHSO_3$

15. [Structure: $H-C(OMe)_3$, trimethyl orthoformate] + [Structure: tetrahydropyran-4-one] $\xrightarrow[20°C, 15 min]{HOH, H^+/catalyst}$ (*A*) + $H-\overset{O}{\overset{||}{C}}-OMe$ (Methyl formate); Product (*A*) is :

(a) [Structure: tetrahydropyran with OH and OMe at C-4] (b) [Structure: tetrahydropyran with OMe, OMe at C-4] (c) [Structure: tetrahydropyran with OMe, Me at C-4] (d) [Structure: tetrahydropyran with Me, Me at C-4]

16. [cyclohexanone] $\xrightarrow{P} \xrightarrow{Q} \xrightarrow{R}$ [bicyclic enone]

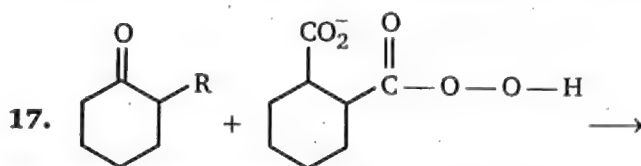
Reagents to carry out above conversion, *P*, *Q*, *R* respectively are :

(a) $H_2C=CH-CH_2-Br, (HO^{\ominus}), [HO^{\ominus}, \Delta]$, Wacker-process

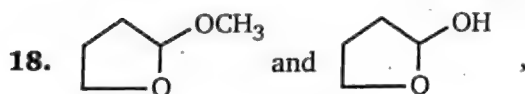
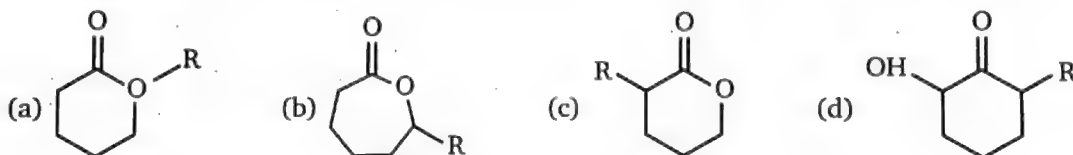
(b) $H_2C=CH-CH_2-Br(HO^{\ominus})$, Wacker-process, $HO^{\ominus}, \Delta$

(c) Wacker process, $H_2C=CH-CH_2-Br(HO^{\ominus}), HO^{\ominus}(\Delta)$

(d) Wacker process, $HO^{\ominus}(\Delta), H_2C=CH-CH_2-Br(HO^{\ominus})$

17. [2-R-cyclohexanone] + [cyclohexane with CO_2^- and C(=O)—O—O—H] $\longrightarrow$

Above reaction is a Baeyer Villiger rearrangement of an asymmetric ketone with magnesium mono peroxo pthalate hexahydrate (in the drawing, Mg^{+2} is omitted for clearity) Identify major product.

(a) [structure] (b) [structure] (c) [structure] (d) [structure]

18. [2-methoxytetrahydrofuran, OCH_3] and [2-hydroxytetrahydrofuran, OH] ,

Above compounds can be differentiated by following reagent:

(a) 2-4 DNP (Brady reagent) (b) Tollen's reagent

(c) Lucas reagent (d) $NaHSO_3$

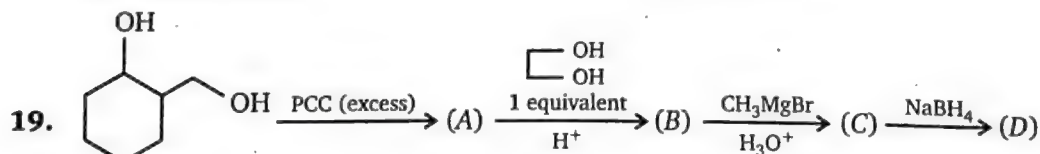
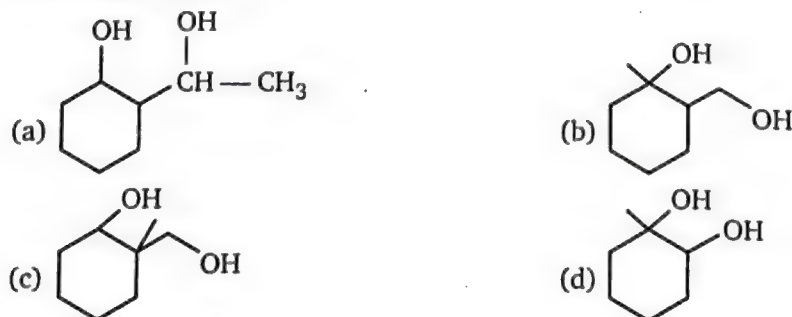
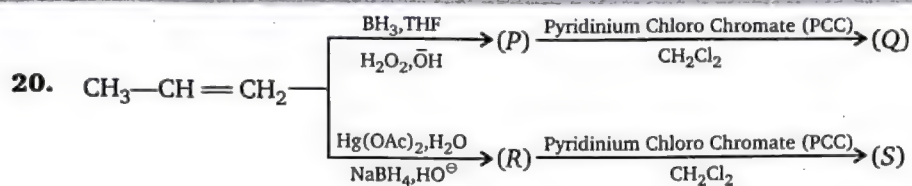
19. [2-(hydroxymethyl)cyclohexanol] $\xrightarrow{\text{PCC (excess)}} (A) \xrightarrow[\text{H}^+]{\text{ethylene glycol, 1 equivalent}} (B) \xrightarrow[\text{H}_3\text{O}^+]{\text{CH}_3\text{MgBr}} (C) \xrightarrow{\text{NaBH}_4} (D)$

Product (*D*) will be :

(a) [structure: OH, CH(OH)—CH_3] (b) [structure: OH, OH]

(c) [structure: OH, OH] (d) [structure: OH, OH]

20. $CH_3—CH=CH_2$ $\xrightarrow[H_2O_2, \bar{O}H]{BH_3, THF}$ (P) $\xrightarrow[CH_2Cl_2]{\text{Pyridinium Chloro Chromate (PCC)}}$ (Q)

$CH_3—CH=CH_2$ $\xrightarrow[NaBH_4, HO^{\ominus}]{Hg(OAc)_2, H_2O}$ (R) $\xrightarrow[CH_2Cl_2]{\text{Pyridinium Chloro Chromate (PCC)}}$ (S)

Relationship between products (Q) and (S) is:

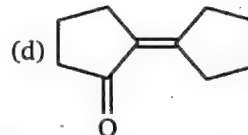
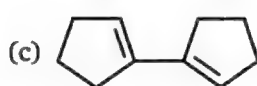
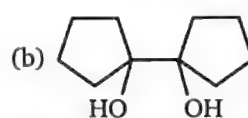
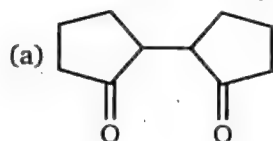
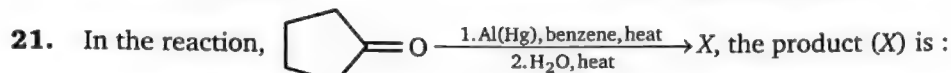
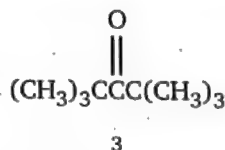
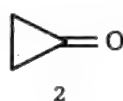
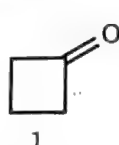
(a) Positional isomer
(b) Chain isomer
(c) Stereoisomer
(d) Functional isomer

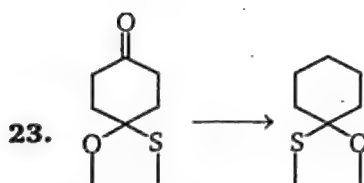
21. In the reaction, (cyclopentanone) $\xrightarrow[2. H_2O, heat]{1. Al(Hg), benzene, heat}$ X, the product (X) is :

(a)

(b) HO OH

(c)

(d)

22. Rank the following in order of increasing value of the equilibrium constant for hydration, $K_{hyd.}$ (smallest value first).

(a) $1 < 2 < 3$
(b) $3 < 1 < 2$
(c) $2 < 1 < 3$
(d) $2 < 3 < 1$

23.

Above conversion can be achieved by:

(a) $Zn(Hg), HCl$
(b) $NH_2—NH_2/KOH/\Delta$
(c) $LiAlH_4$
(d) H_2/Ni

24. Which sequence represents the best synthesis of hexanal ?

$$CH_3CH_2CH_2CH_2CH_2CH=O$$
Hexanal

(a) 1. $CH_3CH_2CH_2\ CH_2Br + NaC\equiv CH$
2. H_2O, H_2SO_4, $HgSO_4$

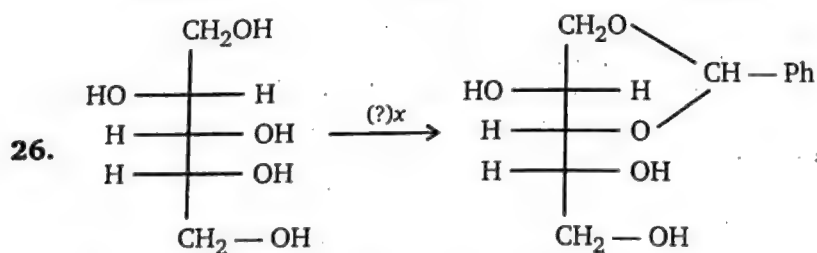
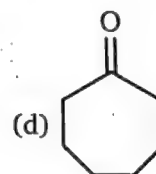
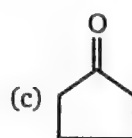
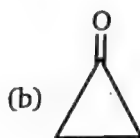
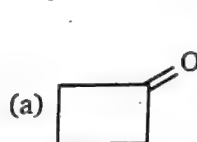
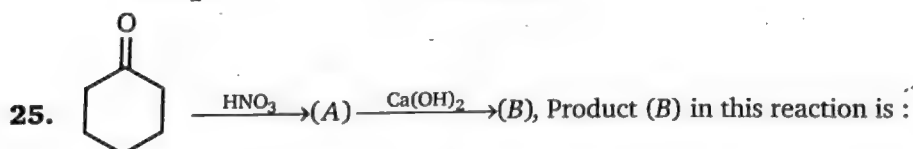
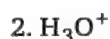
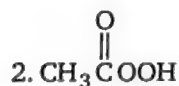
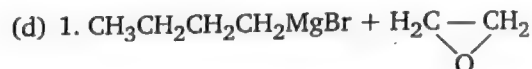
(b) 1. $CH_3CH_2CH_2CH=CH_2 + CH_3\overset{O}{\overset{\|}{C}}OOH$
2. CH_3MgBr, diethyl ether
3. H_3O^+
4. PCC, CH_2Cl_2

(c) 1. $CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$
2. $CH_3\overset{O}{\overset{\|}{C}}OOH$ 3. $LiAlH_4$
4. H_2O 5. PCC, CH_2Cl_2

(d) 1. $CH_3CH_2CH_2CH_2MgBr$ + $H_2C - CH_2$ (with O bridging, epoxide)
2. H_3O^+ 3. PCC, CH_2Cl_2

25.

(a) (b) (c) (d)

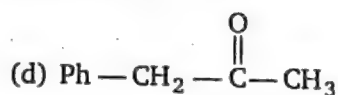
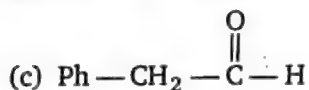
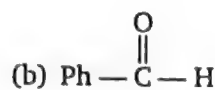
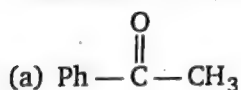
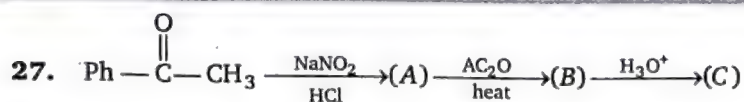
26.

Compound (x) in the above reaction is :

(a) $Ph-\overset{O}{\overset{\|}{C}}-CH_3$

(b) $Ph-\overset{O}{\overset{\|}{C}}-H$

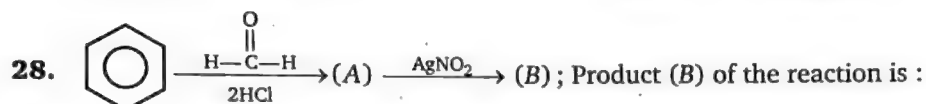
(c) $Ph-CH_2-\overset{O}{\overset{\|}{C}}-H$

(d) $Ph-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

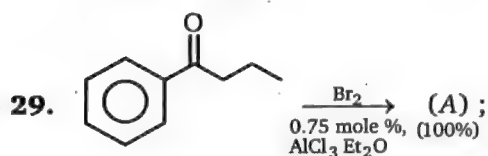
27. $Ph-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[HCl]{NaNO_2} (A) \xrightarrow[heat]{AC_2O} (B) \xrightarrow{H_3O^+} (C)$

Product (*C*) of the above reaction is :

(a) $Ph-CO_2H$ (b) $Ph-\overset{O}{\overset{\|}{C}}-CO_2H$

(c) $Ph-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$ (d) $Ph-\overset{O}{\overset{\|}{C}}-CH_2OH$

28. (benzene) $\xrightarrow[2HCl]{H-\overset{O}{\overset{\|}{C}}-H} (A) \xrightarrow{AgNO_2} (B)$; Product (*B*) of the reaction is :

(a) $Ph-CH_2-NO_2$ (b) $Ph-CH_2-ONO$

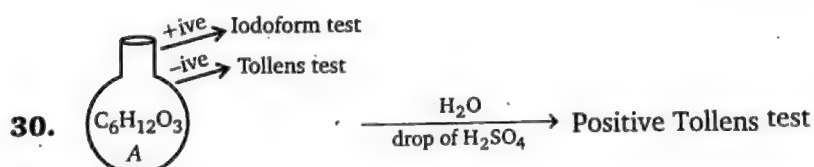
(c) $Ph-CHO$ (d) $Ph-O-N=O$

29. (structure with O) $\xrightarrow[\text{0.75 mole \%, } AlCl_3\ Et_2O]{Br_2} (A)$; (100%)

Product (*A*) of the above reaction is (bromination occur not in the benzene ring) :

(a) (structure with O, Br) (b) (structure with O, Br)

(c) (structure with O, Br) (d) (structure with $\overset{O}{\overset{\|}{C}}$, Br, CH_3)

30. $C_6H_{12}O_3$ (*A*): +ive → Iodoform test; -ive → Tollens test

$\xrightarrow[\text{drop of } H_2SO_4]{H_2O}$ Positive Tollens test

Compound (*A*) is :

(a) $CH_3-\overset{O}{\overset{\|}{C}}-\underset{OCH_3}{\underset{|}{CH}}-\underset{OCH_3}{\underset{|}{CH_2}}$ (b) $CH_3-\overset{O}{\overset{\|}{C}}-\overset{OCH_3}{\overset{|}{\underset{OCH_3}{\underset{|}{C}}}}-CH_3$

(c) $CH_3-\overset{\overset{O}{||}}{C}-CH_2-\underset{\underset{OCH_3}{|}}{CH}-OCH_3$ (d) $H-\overset{\overset{O}{||}}{C}-CH_2-CH_2-\underset{\underset{OCH_3}{|}}{CH}-OCH_3$

31. $\underset{(A)}{C_{16}H_{16}} \xrightarrow{O_3} \underset{C_8H_8O}{(B)} \xrightarrow[HO^-/\Delta]{NH_2-NH_2}$ (ethylbenzene) ; Reactant (*A*) in this reaction is :

(a) $(Ph)_2C=C(CH_3)_2$

(b) $\underset{CH_3}{\overset{Ph}{>}}C=C\underset{Ph}{\overset{CH_3}{<}}$

(c) $\underset{CH_3}{\overset{Ph}{>}}C=C\underset{CH_3}{\overset{Ph}{<}}$

(d) both (b) and (c)

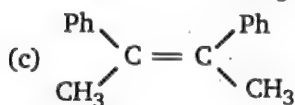
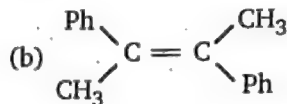
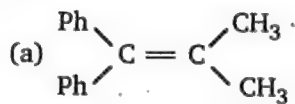
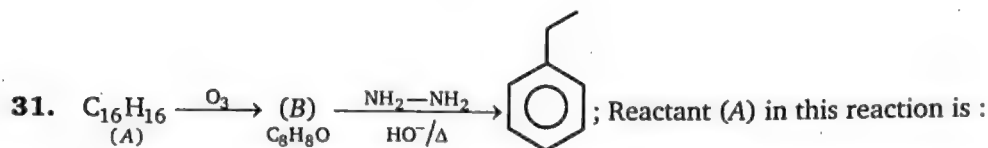
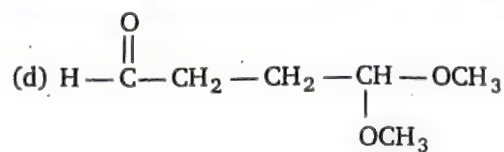
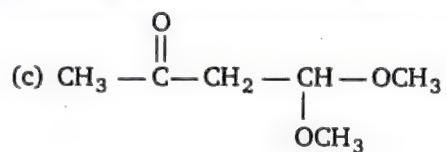
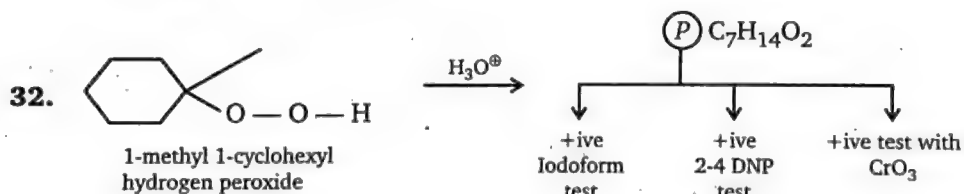
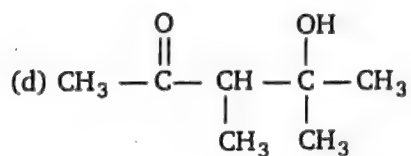
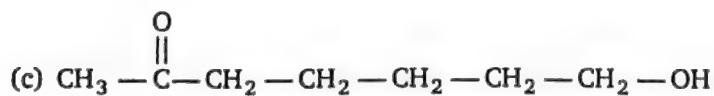
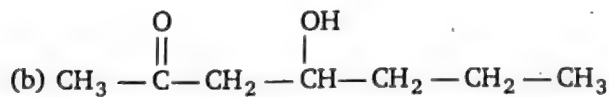
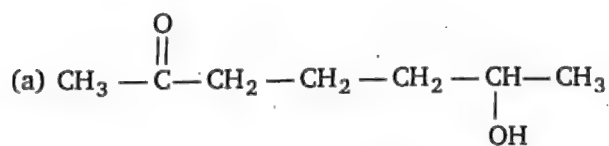
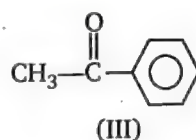
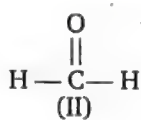
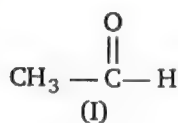
32.

Compound (*P*) is :

(a) $CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$

(b) $CH_3-\overset{\overset{O}{||}}{C}-CH_2-\overset{\overset{OH}{|}}{CH}-CH_2-CH_2-CH_3$

(c) $CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2-CH_2-CH_2-CH_2-OH$

(d) $CH_3-\overset{\overset{O}{||}}{C}-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

33. Correct order of reactivity of following compounds towards Grignard reagent?

$CH_3-\overset{O}{\overset{||}{C}}-H$ (I) $H-\overset{O}{\overset{||}{C}}-H$ (II) $CH_3-\overset{O}{\overset{||}{C}}-C_6H_5$ (III)

(a) I > II > III (b) II > I > III (c) II > III > I (d) I > III > II

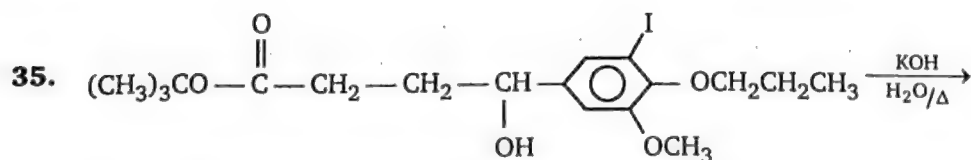
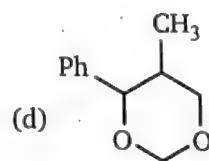
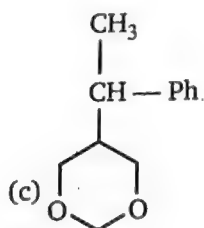
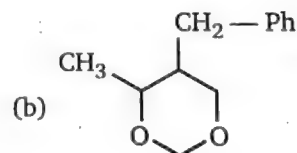
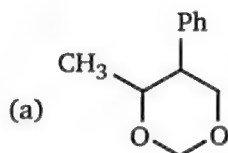
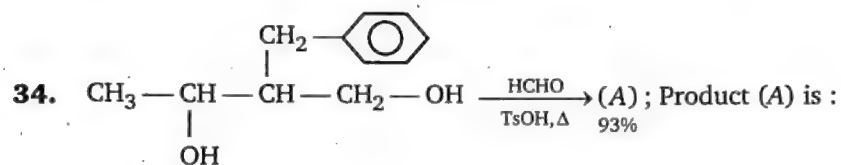
34. $CH_3-\underset{OH}{\underset{|}{CH}}-\overset{CH_2-C_6H_5}{\overset{|}{CH}}-CH_2-OH \xrightarrow[TsOH,\Delta]{HCHO} (A)$; Product (A) is : 93%

(a) 1,3-dioxane ring with CH_3 and Ph substituents

(b) 1,3-dioxane ring with CH_3 and CH_2-Ph substituents

(c) 1,3-dioxane ring with $CH(CH_3)-Ph$ substituent

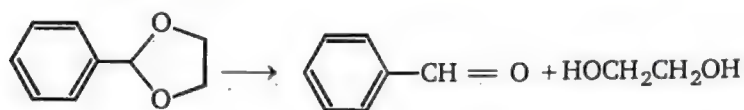
(d) 1,3-dioxane ring with Ph and CH_3 substituents

35. $(CH_3)_3CO-\overset{O}{\overset{||}{C}}-CH_2-CH_2-\underset{OH}{\underset{|}{CH}}-C_6H_2(I)(OCH_3)-OCH_2CH_2CH_3 \xrightarrow[H_2O/\Delta]{KOH}$

Total number of products obtained in above reaction is :

(a) 2 (b) 3

(c) 4 (d) 5

36. What reagent and/or reaction conditions would you choose to bring about the following conversion?

$\longrightarrow$ —CH = O + $HOCH_2CH_2OH$

(a) 1. $LiAlH_4$, 2. H_2O (b) H_2O, H_2SO_4, heat

(c) H_2O, NaOH, heat (d) PCC, CH_2Cl_2

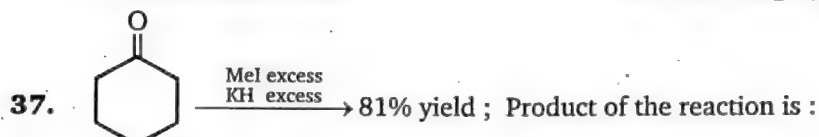
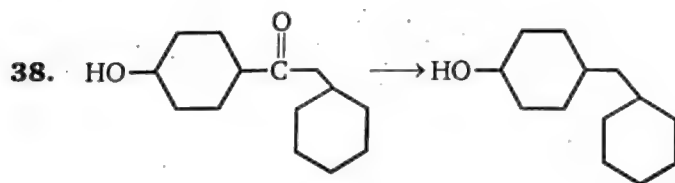
37. $\xrightarrow[\text{KH excess}]{\text{MeI excess}}$ 81% yield ; Product of the reaction is :

(a)

(b)

(c)

(d)

38. HO— —C(=O)— $\longrightarrow$ HO—

The above reduction can be best carried out by :

(a) Clemmensen reduction (b) Wolff-Kishner reduction

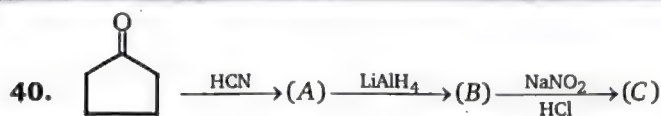
(c) $NaBH_4$ (d) None of these

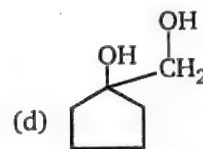
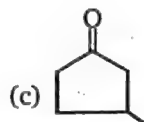
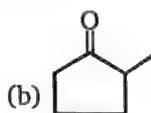
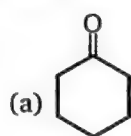
39. $CH_3-C\equiv CH \xrightarrow[\text{dil. } H_2SO_4]{HgSO_4} (A)$

$CH_3-C\equiv CH \xrightarrow[(2)\, H_2O_2/HO^-]{(1)\, BH_3\cdot THF} (B)$

Product (A) and (B) is differentiated by:

(a) 2-4-DNP (b) NaOI (c) Na-metal (d) $NaHSO_3$

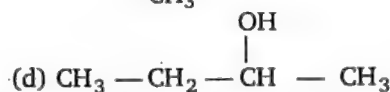
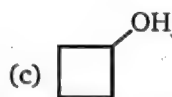
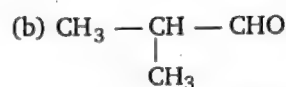
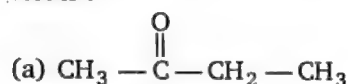
40. (cyclopentanone) $\xrightarrow{HCN} (A) \xrightarrow{LiAlH_4} (B) \xrightarrow[HCl]{NaNO_2} (C)$

End product (*C*) in above reaction is :

(a) (b) (c) (d)

41. Compound (*X*) C_4H_8O, which reacts with 2, 4-DNP derivative and gives negative haloform test is :

(a) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

(b) $CH_3-\underset{CH_3}{\underset{|}{CH}}-CHO$

(c)

(d) $CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-CH_3$

42. When a nucleophile encounters a ketone, the site of attack is :

(a) the carbon atom of the carbonyl

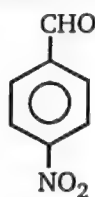
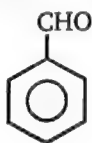
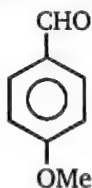
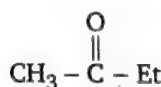
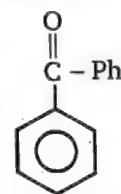
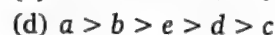
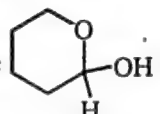
(b) the oxygen atom of the carbonyl

(c) both the carbon and oxygen atoms, with equal probability

(d) no attack occurs as ketones do not react with nucleophiles

43. The correct order of rate of reaction toward nucleophilic addition reaction:

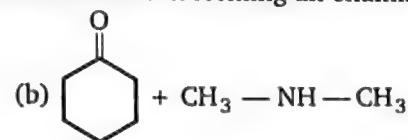
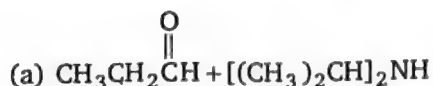
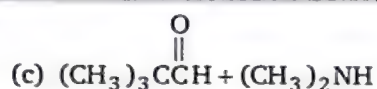
(a) $a > b > c > d > e$ (b) $a > b > d > c > e$

(c) $a > d > e > b > c$ (d) $a > b > e > d > c$

44. The structure (tetrahydropyran ring with H and OH on the carbon next to O) would be best classified as a(an) :

(a) Acetal (b) Hemiacetal (c) Hydrate (d) Cyanohydrin

45. Which of the following pairs of reactants is most effective in forming an enamine ?

(a) $CH_3CH_2\overset{O}{\overset{\|}{C}}H + [(CH_3)_2CH]_2NH$

(b) (cyclohexanone) $+ CH_3-NH-CH_3$

(c) $(CH_3)_3C\overset{O}{\overset{\|}{C}}H + (CH_3)_2NH$ (d) None of these form an enamine.

46. The reaction of $C_6H_5CH = CHCHO$ with $LiAlH_4$ gives :

(a) $C_6H_5CH_2CH_2CH_2OH$ (b) $C_6H_5CH = CHCH_2OH$

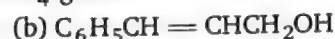
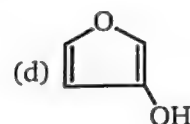
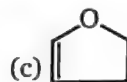
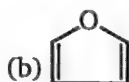
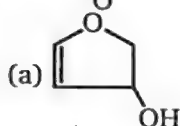
(c) $C_6H_5CH_2CH_2CHO$ (d) $C_6H_5CH_2CHOHCH_3$

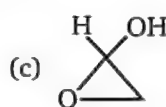
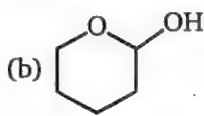
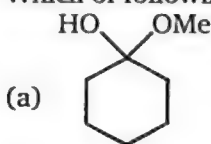
47.

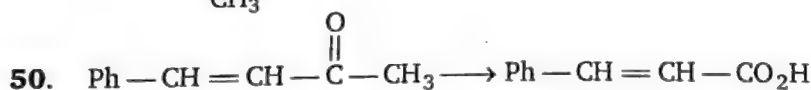
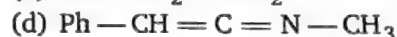
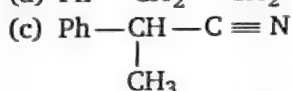
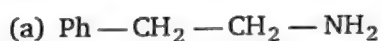
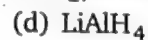
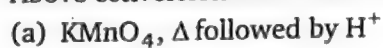
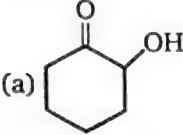
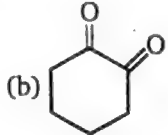
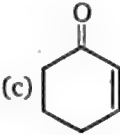
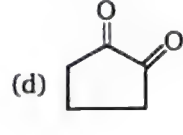
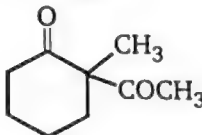
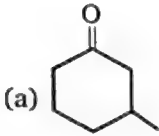
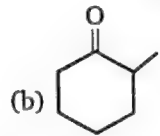
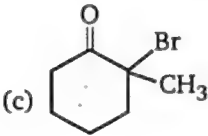
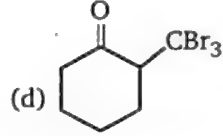
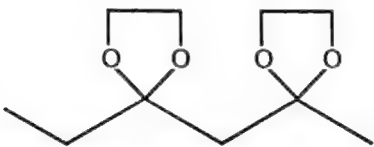
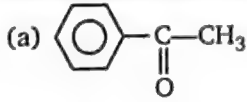
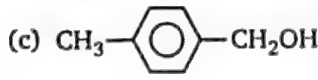
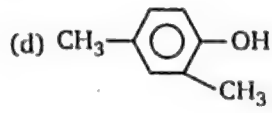
(a)

(b)

(c)

(d) OH

48. Which of following compound is hemiacetal ?

(a)

(b) O OH (c) H OH O (d) all of these

49. $Ph-CH_2-C\equiv N \xrightarrow[THF]{LDA} \xrightarrow{CH_3I} 71\%$; End product of the reaction will be :

(a) $Ph-CH_2-CH_2-NH_2$ (b) $Ph-CH_2-NH_2$

(c) $Ph-\underset{CH_3}{\underset{|}{CH}}-C\equiv N$ (d) $Ph-CH=C=N-CH_3$

50. $Ph-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow Ph-CH=CH-CO_2H$

Above conversion can be achieved by :

(a) $KMnO_4$, Δ followed by H^+ (b) $I_2/NaOH$ followed by H^+

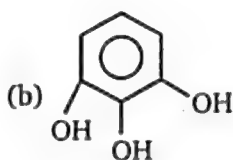
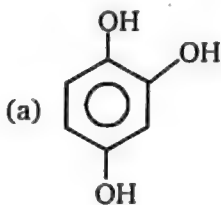
(c) H_2/Pt (d) $LiAlH_4$

51. OH, O, O—CH_2 $\xrightarrow{H_3O^{\oplus}}$ Products ; Product of the reaction is/are :

(a)

(b) OH OH OH (c) HCHO (d) Both (a) and (c)

52. Cyclohexanone $\xrightarrow{SeO_2}$ (*A*); Product (*A*) of the reaction is :

(a) 2-hydroxycyclohexanone (b) cyclohexane-1,2-dione (c) cyclohex-2-enone (d) cyclopentane-1,2-dione

53. 2-Acetyl-2-methylcyclohexanone (ring C=O with CH_3 and $COCH_3$) $\xrightarrow[\Delta]{Br_2+NaOH}$ (*A*) + $CHBr_3$; Product (*C*) of the reaction is :

(*A*) $\xrightarrow[\Delta]{H^+}$ (*C*)

(a) 3-methylcyclohexanone (b) 2-methylcyclohexanone (c) 2-bromo-2-methylcyclohexanone (Br, CH_3) (d) 2-(CBr_3)cyclohexanone

54. Bis(ethylene ketal) $\xrightarrow{H_3O^{\oplus}}$ (*A*) + 2 Glycol

Product (*A*) of the reaction will be :

(a) $CH_3-CH_2-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-CH_2-CH_3$

(b) $CH_3-CH_2-\overset{O}{\overset{||}{C}}-CH_2-CH_2-\overset{O}{\overset{||}{C}}-CH_3$

(c) $CH_3-CH_2-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-CH_3$

(d) $CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-CH_3$

55. $R-\overset{O}{\overset{||}{C}}-H \xrightarrow{R-NH_2} R-CH=N-R$. This reaction gives best yield at :

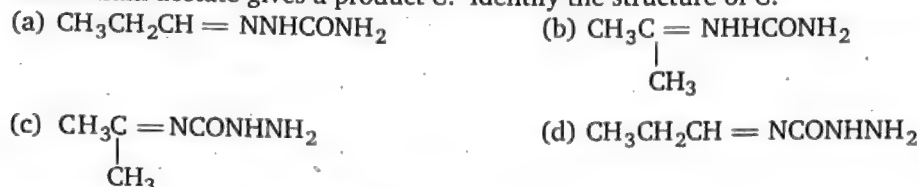
(a) pH 1 - 2 (b) pH 4 - 5 (c) pH 10 - 11 (d) pH 13 - 14

56. An aromatic compound *A* of the molecular formula $C_8H_{10}O$ on reaction with iodine and dilute NaOH gives a yellow precipitate. The structure of the compound is expected to be:

(a) $C_6H_5-\overset{||}{\underset{O}{C}}-CH_3$ (b) $C_6H_5CHOHCH_3$

(c) $CH_3-C_6H_4-CH_2OH$ (d) $CH_3-C_6H_3(CH_3)-OH$

57. Compound A (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product B(molecular formula C_3H_6O). B forms a shining silver mirror on warming with ammonical silver nitrate, B when treated with an aqueous solution of $NH_2NHCONH_2$ and sodium acetate gives a product C. Identify the structure of C.

(a) $CH_3CH_2CH=NNHCONH_2$
(b) $CH_3C(CH_3)=NHHCONH_2$
(c) $CH_3C(CH_3)=NCONHNH_2$
(d) $CH_3CH_2CH=NCONHNH_2$

58. In the reaction, the acid obtained will be :

$CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN \xrightarrow{H-OH} CH_3CH(OH)COOH$

(a) D-isomer
(b) L-isomer
(c) (80%D + 20%L) mixture
(d) (50%D + 50%L) mixture

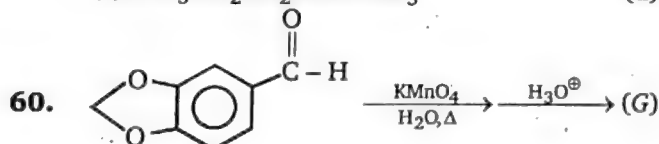
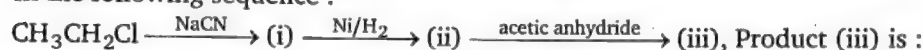
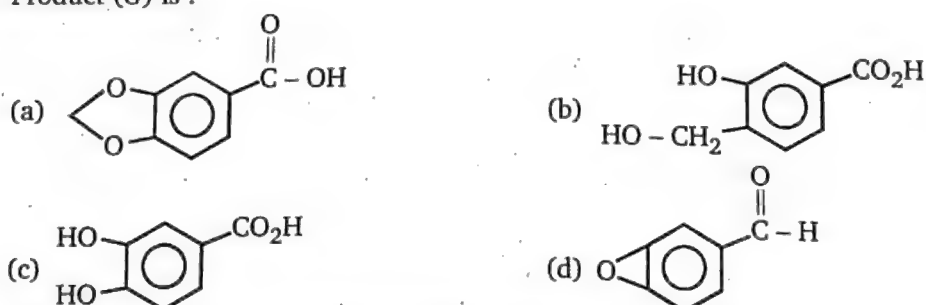
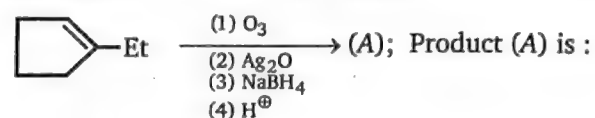
59. In the following sequence :

$CH_3CH_2Cl \xrightarrow{NaCN} (i) \xrightarrow{Ni/H_2} (ii) \xrightarrow{\text{acetic anhydride}} (iii)$, Product (iii) is :

(a) $CH_3CH_2CH_2NH_2$
(b) $CH_3CH_2CH_2CONHCH_3$
(c) $CH_3CH_2CH_2NHCOCH_3$
(d) $CH_3CH_2CH_2CONHCOCH_3$

60. (3,4-methylenedioxybenzaldehyde, C–H with C=O) $\xrightarrow[H_2O,\Delta]{KMnO_4} \xrightarrow{H_3O^{\oplus}} (G)$

Product (G) is :

(a) 3,4-methylenedioxy benzoic acid (C(=O)–OH)
(b) HO–, HO–CH$_2$– substituted benzene with CO_2H
(c) HO–, HO– substituted benzene with CO_2H
(d) O-bridged benzene with C(=O)–H

61. Carbonyl compounds can generally be converted to hydrocarbons by :

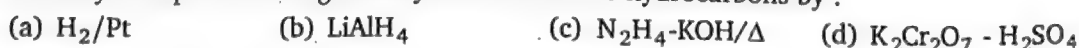
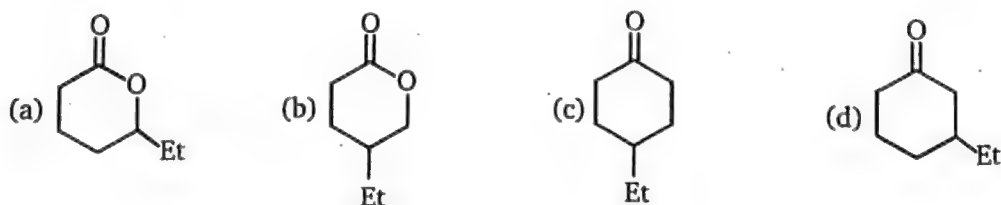
(a) H_2/Pt
(b) $LiAlH_4$
(c) N_2H_4-KOH/Δ
(d) $K_2Cr_2O_7$ - H_2SO_4

62. (cyclopentene)–Et $\xrightarrow[(2)\ Ag_2O\ (3)\ NaBH_4\ (4)\ H^{\oplus}]{(1)\ O_3}$ (A); Product (A) is :

(a)

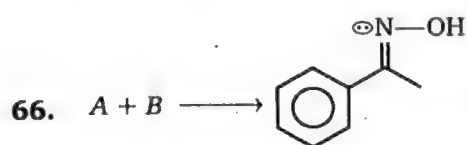
(b)

(c)

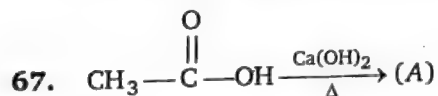
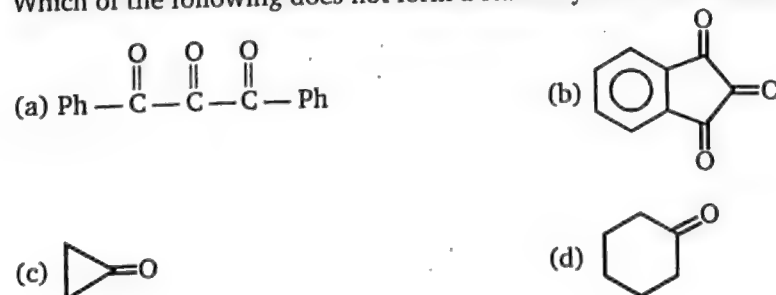
(d)

63. Which statement about the aldol condensation is correct ?
(a) A Lewis acid is commonly used as a catalyst
(b) The initial step is probably the formation of a carbanion
(c) A Lewis base is employed to induce carbocation formation
(d) The carbon chain is lengthened through the elimination of 1 mole of water

64. A compound gives a positive test with $I_2/NaOH$ and is extracted from benzene by saturated $NaHSO_3$. It may be :
(a) $CH_3(CH_2)_4CHO$ (b) $CH_3(CH_2)_3COCH_3$
(c) $CH_3CH_2COCH_2CH_3$ (d) $CH_3(CH_2)_4CH_2OH$

65. Which of the following compounds on reaction with excess CH_3MgBr and subsequent hydrolysis will give a tertiary alcohol?
(a) C_2H_5CHO (b) $C_2H_5CO_2CH_3$ (c) C_2H_5COOH (d) $CH_3CH—CHCH_3$ (epoxide, bridged by O)

66. $A + B \longrightarrow$ $C_6H_5—C(=N—OH)—CH_3$

Reactant (A) and (B) is :
(a) $Ph—CH_2—CH=O + NH_2—OH$ (b) $Ph—CH=O + NH_2—OH$
(c) $Ph—\overset{O}{\overset{\|}{C}}—CH_3 + NH_2—NH_2$ (d) $Ph—\overset{O}{\overset{\|}{C}}—CH_3 + NH_2—OH$

67. $CH_3—\overset{O}{\overset{\|}{C}}—OH \xrightarrow[\Delta]{Ca(OH)_2} (A)$

Product (A) is :
(a) $CH_3CH_2CH=O$ (b) CH_3COCH_3
(c) $CH_3CH(OH)CH_3$ (d) $CH_3CH_2CH_2OH$

68. Which of the following does not form a stable hydrate on addition of H_2O ?
(a) $Ph—\overset{O}{\overset{\|}{C}}—\overset{O}{\overset{\|}{C}}—\overset{O}{\overset{\|}{C}}—Ph$ (b)
(c) (d) cyclohexanone

69. Consider the following sequence of reactions.

Ketone $A \xrightarrow[2. H_2O]{1. C_2H_5MgBr} B \xrightarrow[-H_2O]{H_2SO_4,\ heat} C \xrightarrow[2.\ Zn,\ H_2O]{1.\ O_3}$ (butan-2-one) + (acetaldehyde, H–C=O)

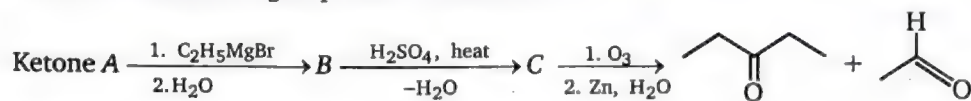
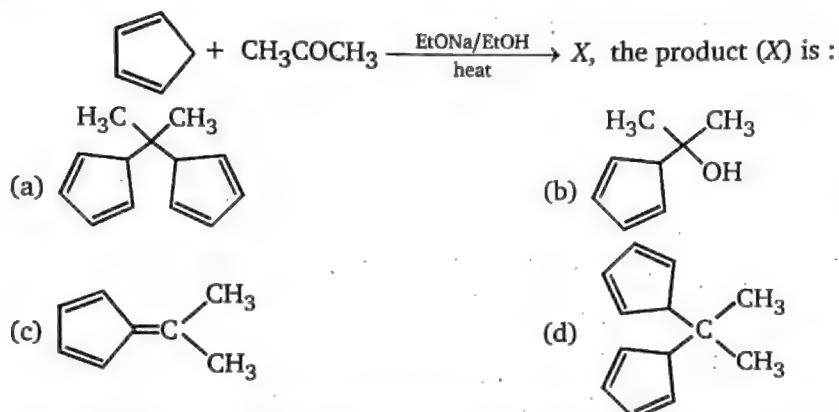
The ketone (*A*) is :

(a) butan-2-one (b) pentan-3-one (c) pentan-2-one (d) acetone

70. In the reaction,

cyclopentadiene + $CH_3COCH_3 \xrightarrow[heat]{EtONa/EtOH} X$, the product (*X*) is :

(a) $(H_3C)(CH_3)C$ bonded to two cyclopentadiene rings (b) cyclopentadiene–$C(H_3C)(CH_3)OH$

(c) cyclopentadiene$=C(CH_3)_2$ (d) two cyclopentadiene rings on $C(CH_3)_2$

71. The conversion of acetophenone into benzoic acid can be achieved by its reaction with :

(a) sodium hydroxide followed by acidification
(b) iodine and sodium hydroxide, followed by acidification
(c) hydroxylamine followed by reaction with H_2SO_4
(d) *m*-chloroperoxobenzoic acid

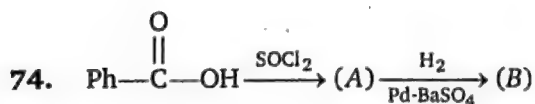
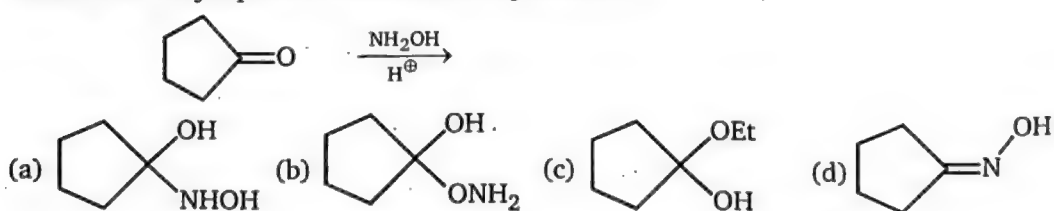
72. In which of the following compounds the methylenic hydrogens are the most acidic ?

(a) $CH_3COCH_2CH_3$ (b) $CH_3CH_2COOC_2H_5$
(c) $CH_3CH_2CH(COOC_2H_5)_2$ (d) CH_3COCH_2CN

73. Which is the major product of the following reaction ?

cyclopentanone (C=O) $\xrightarrow[H^{\oplus}]{NH_2OH}$

(a) cyclopentane with OH and NHOH on the same carbon (b) cyclopentane with OH and ONH_2 on the same carbon (c) cyclopentane with OEt and OH on the same carbon (d) cyclopentane=N–OH

74. $Ph-\overset{O}{\overset{||}{C}}-OH \xrightarrow{SOCl_2} (A) \xrightarrow[Pd\text{-}BaSO_4]{H_2} (B)$

Product (*B*) is :

(a) $Ph-\overset{O}{\overset{||}{C}}-H$ (b) $Ph-CH_2-OH$
(c) $Ph-CH_2-Cl$ (d) $Ph-CH=CH_2$

75. The presence of unsaturation in organic compounds can be tested with :
(a) Schiff's reagent (b) Tollens' reagent (c) Fehling's reagent (d) Baeyer's reagent

76. Which of the following gives iodoform test ?
(a) CH_3CH_2OH (b) C_2H_5CHO (c) $(CH_2OH)_2$ (d) None of these

77. Which of the following β-keto carboxylic acid does not undergo decarboxylation on heating ?

(a)

(b) CO_2H $=O$

(c)

(d) None of these

78. $HOCH_2CH_2CH_2-\overset{O}{\overset{||}{C}}-OCH_2CH_3 \xrightarrow{PCC} (A) \xrightarrow[\text{(1 molar equivalent)}]{H_2C=CHMgBr} (B) \xrightarrow{NH_4Cl/H_2O} (C)$

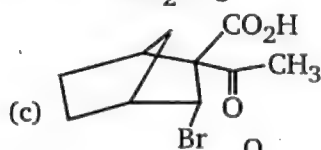
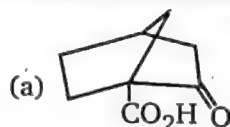
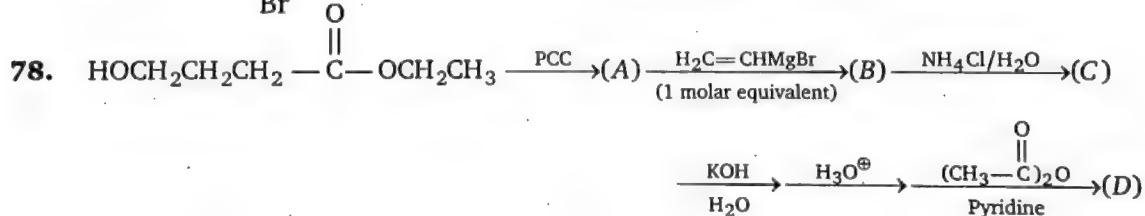
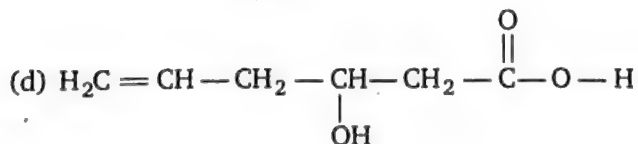
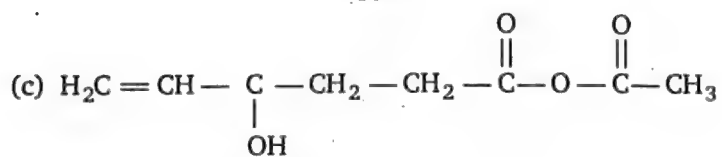
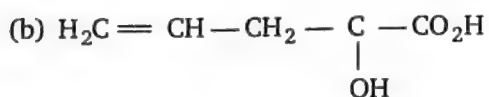
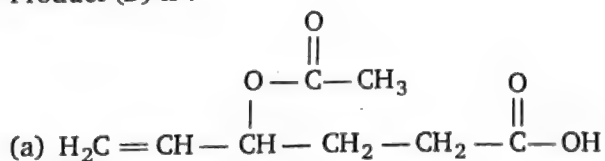
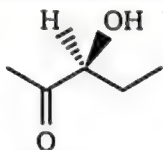
$\xrightarrow[H_2O]{KOH} \xrightarrow{H_3O^{\oplus}} \xrightarrow[\text{Pyridine}]{(CH_3-\overset{O}{\overset{||}{C}})_2O} (D)$

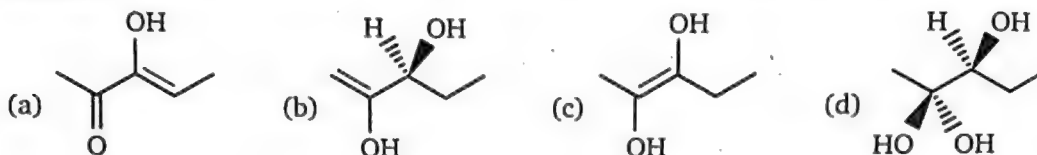
Product (*D*) is :

(a) $H_2C=CH-\underset{O-\overset{O}{\overset{||}{C}}-CH_3}{CH}-CH_2-CH_2-\overset{O}{\overset{||}{C}}-OH$ (the $O-C(=O)-CH_3$ group attached to the third carbon)

(b) $H_2C=CH-CH_2-\underset{OH}{\underset{|}{C}}-CO_2H$

(c) $H_2C=CH-\underset{OH}{\underset{|}{C}}-CH_2-CH_2-\overset{O}{\overset{||}{C}}-O-\overset{O}{\overset{||}{C}}-CH_3$

(d) $H_2C=CH-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{||}{C}}-O-H$

79. The compound shown in the below undergoes racemization on reaction with aqueous acid.

Which of the following structures best represents the intermediate responsible for this process?

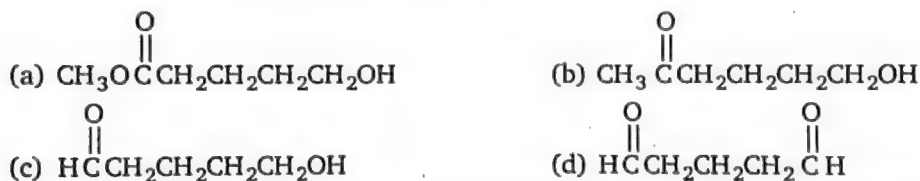
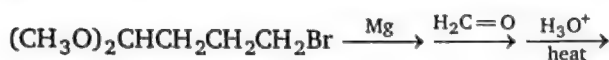
(a) (b) (c) (d)

80. The final product of the following sequence of reaction is :

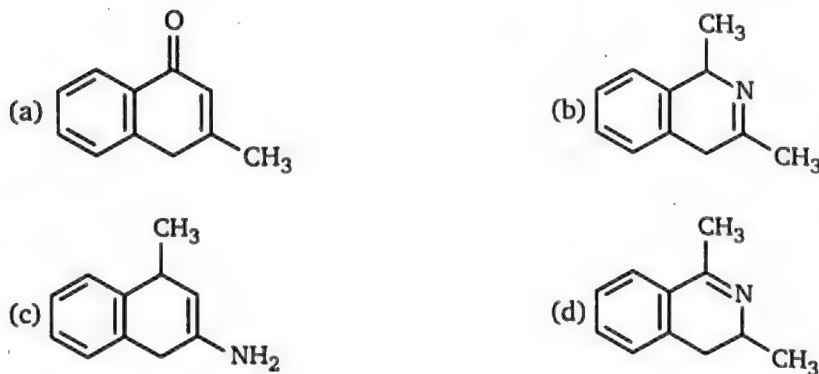
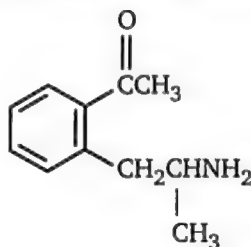
$$(CH_3O)_2CHCH_2CH_2CH_2Br \xrightarrow{Mg} \xrightarrow{H_2C=O} \xrightarrow[heat]{H_3O^+}$$

(a) $CH_3O\overset{O}{\overset{||}{C}}CH_2CH_2CH_2CH_2OH$

(b) $CH_3\overset{O}{\overset{||}{C}}CH_2CH_2CH_2CH_2OH$

(c) $H\overset{O}{\overset{||}{C}}CH_2CH_2CH_2CH_2OH$

(d) $H\overset{O}{\overset{||}{C}}CH_2CH_2CH_2\overset{O}{\overset{||}{C}}H$

81. The amino ketone shown below undergoes a spontaneous cyclization on standing. What is the major product of this intramolecular reaction ?

(a) (b) (c) (d)

82. Compound (*A*) $C_6H_{12}O$ is optically active. Compound (*A*) give negative Tollens test and positive test with 2-4-di-nitro phenyl hydrazine. Identify *A*.

(a) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

(b) $CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_2-CH_3}{|}}{CH}-CH_3$

(c) $H-\overset{\overset{O}{\|}}{C}-CH_2-\underset{\underset{CH_2-CH_3}{|}}{CH}-CH_3$

(d) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-CH_3$

83. N + Me NO_2 $\xrightarrow[(2)\,H_3O^{\oplus}]{(1)\,Et_2O}$ (*A*) ; Product (*A*) of the reaction is :
99%

(a) O NO_2

(b) O NO_2

(c) O NO_2

(d) O NO_2

84.

(*N*) $\xrightarrow[H_2O]{NH_4Cl}$ (*O*) $\xrightarrow[\text{cold}]{HCl\,(conc.)}$ (*P*) $\xrightarrow[\text{ethanol},\,\Delta]{KOH\,(4\ molar)}$ (*Q*)

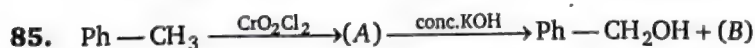
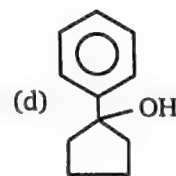
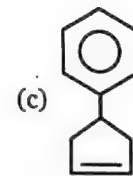
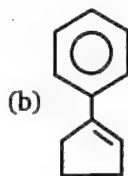
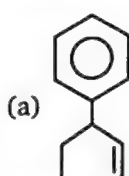
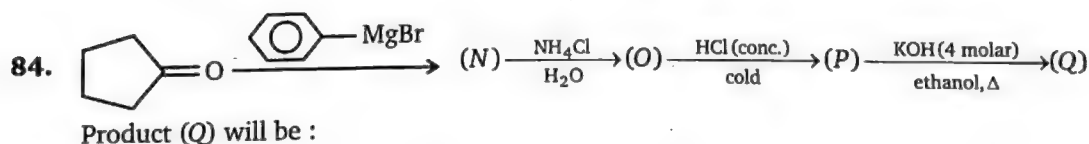
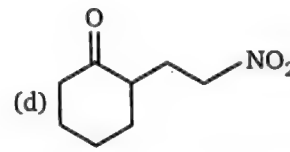
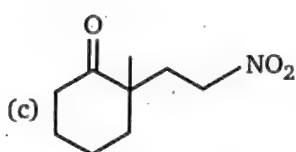
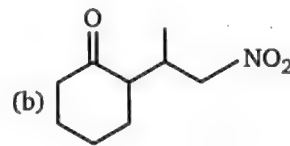
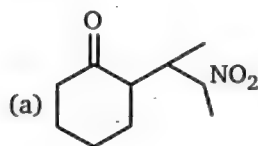
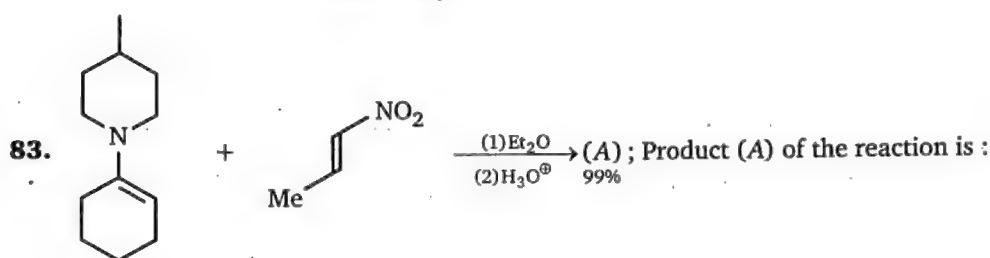
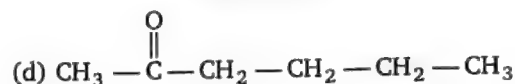
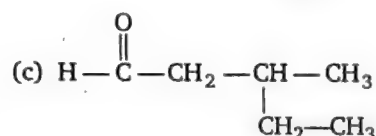
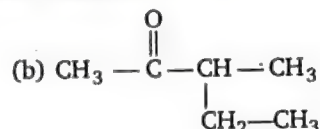
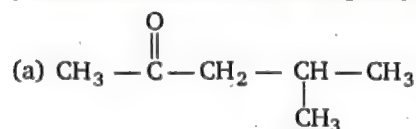
Product (*Q*) will be :

(a)

(b)

(c)

(d)

85. $Ph-CH_3 \xrightarrow{CrO_2Cl_2} (A) \xrightarrow{conc.KOH} Ph-CH_2OH + (B)$

Product (*B*) of above the reaction is :

(a) $Ph-CO_2H$ (b) $Ph-CO_2^-$ (c) $Ph-CHO$ (d) $Ph-CH_3$

86. Fischer projection: CHO on top; H —C— OH; CH_2-OH at bottom

D-(+)-Glyceraldehyde $\xrightarrow[\text{(ii) } H^+]{\text{(i) KCN}}$ Product ; Product obtained in the reaction is :

(a) Diastereomer (b) Racemic

(c) Meso (d) Optically pure enantiomer

87. Cyclopentanone $\xrightarrow{NH_2OH} (A) \xrightarrow{H^+} (B) \xrightarrow{LAH} (C)$; Product (C) of the reaction is :

(a) piperidine ring with OH at C-4, N–H (b) piperidine, N–H (c) piperidine ring with OH at C-2, N–H (d) piperidine ring with OH at C-2, N–H

88. Cyclopentyl$-\overset{14}{C}\equiv N$ $+ CH_3MgBr \xrightarrow{H_3O^\oplus} (A) \xrightarrow{NaOI} (B)+(C)$

Product (A) and (C) is :

(a) Cyclopentyl$-\overset{O}{\overset{\|}{C}}-CH_3$; CHI_3

(b) Cyclopentyl$-\overset{O}{\overset{\|}{C}}-CH_3$; $\overset{14}{C}HI_3$

(c) Cyclopentyl$-\underset{14}{\overset{O}{\overset{\|}{C}}}-CH_3$; CHI_3

(d) Cyclopentyl$-CH_2-\underset{14}{C}HO$; CHI_3

89. $Ph-\overset{OH}{\overset{|}{C}H}-CH_3 \xrightarrow{PCC} (A) \xrightarrow{NH_2-NH-\overset{O}{\overset{\|}{C}}-NH_2} (B)$

Product (B) is :

(a) $Ph-\overset{CH_3}{\overset{|}{C}}=N-\overset{O}{\overset{\|}{C}}-NH-NH_2$

(b) $Ph-\underset{CH_3}{\underset{|}{C}}=N-NH-\overset{O}{\overset{\|}{C}}-NH_2$

(c) $Ph-CH=N-\underset{CH_3}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-NH_2$

(d) $Ph-CH=N-\overset{O}{\overset{\|}{C}}-NH_2$

90. Cyclohexanone $\xrightarrow[H^{\oplus}]{2EtOH}$ (*P*)

Product (*P*) is :

(a) Hemiacetal (b) Acetal (c) Alcohol (d) Alkane

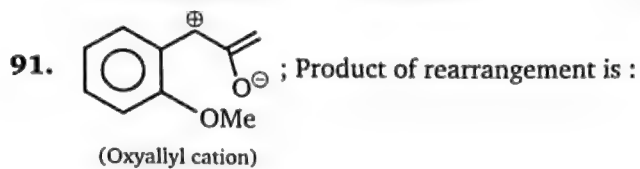
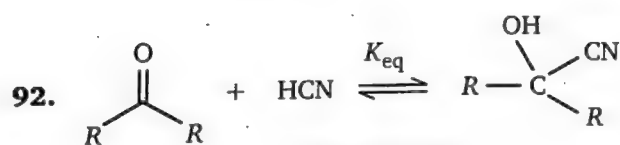
91. (Oxyallyl cation) ; Product of rearrangement is :

(a) [2-methoxyphenyl with methylenecyclopropane, =CH_2, OMe]

(b) [2-methoxyphenyl with epoxide, O, OMe]

(c) [2-methoxyphenyl with cyclopropanone, =O, OMe]

(d) [2-methoxyphenyl with methylenecyclopropane, =CH_2, OMe]

92. $R-CO-R$ + HCN $\overset{K_{eq}}{\rightleftharpoons}$ $R-C(OH)(CN)-R$

Reactant	$K_{eq.}$
PhCHO	*a*
$CH_3COCH_2CH_3$	*b*
$Ph-\overset{O}{\overset{\|\|}{C}}-CH_3$	*c*
$CH_3-\overset{O}{\overset{\|\|}{C}}-H$	*d*

The correct order of decreasing value of $K_{eq.}$ is :

(a) $a > b > c > d$ (b) $d > a > b > c$

(c) $d > b > a > c$ (d) $d > a > c > d$

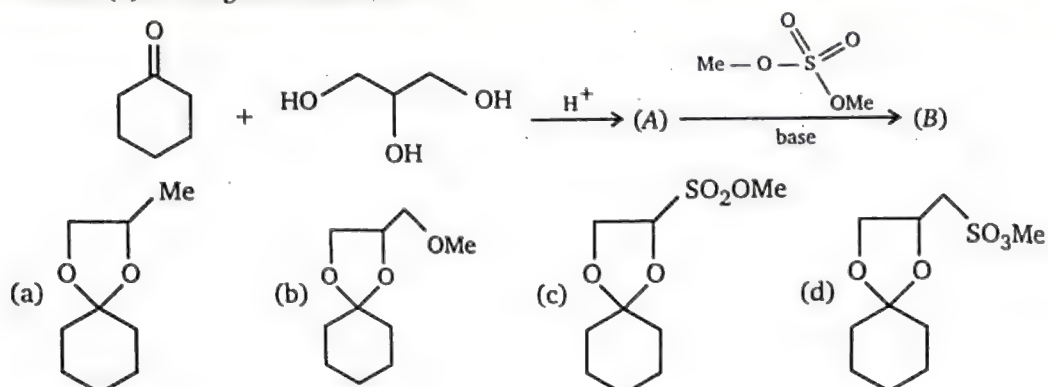
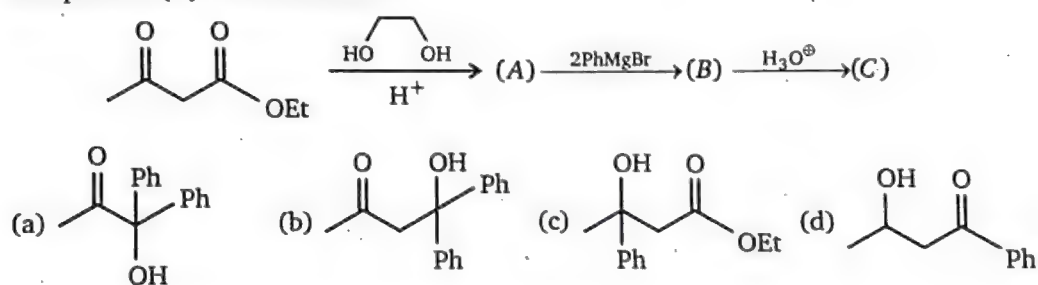
93. Product (*B*) of the given reaction is :

Cyclohexanone + HO–CH₂–CH(OH)–CH₂–OH $\xrightarrow{H^+}$ (*A*) $\xrightarrow[\text{base}]{Me-O-SO_2-OMe}$ (*B*)

(a) Me (b) OMe (c) SO_2OMe (d) SO_3Me

94. End product (*C*) of the reaction is :

OEt $\xrightarrow[H^+]{HO \quad OH}$ (*A*) $\xrightarrow{2PhMgBr}$ (*B*) $\xrightarrow{H_3O^{\oplus}}$ (*C*)

(a) Ph, Ph, OH (b) OH, Ph, Ph (c) OH, Ph, OEt (d) OH, Ph

95. (*A*) $C_{11}H_8O$ → does not undergo self aldol condensation

(*A*) $\xrightarrow{O_3}$ Ph — CHO + 2b $\xrightarrow{Ag^+}$ oxalic acid

Compound (*A*) will be :

(a) Ph — C ≡ C — C ≡ C — CHO (b) Ph — C ≡ C — CH = CH — CHO

(c) Ph — CH = CH — C ≡ C — CHO (d) Ph — CH = CH — C = CH — CO_2H

96. Acetone $\xrightarrow[\text{Catalyst TsOH, 0°C, 2h (molecular sieves)}]{\text{>—OH}}$ Product; Product of the reaction is : (62% yield)

97. Which pair of reactants compounds may be used to make given acetal ?

(a) + CH_2-OH | CH_2-OH (b) + OH OH

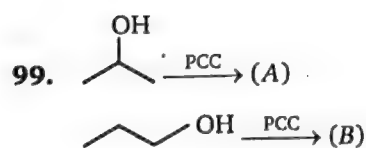
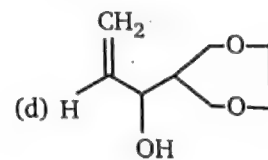
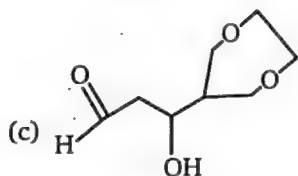
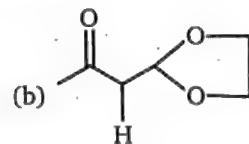
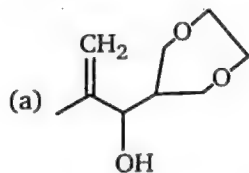
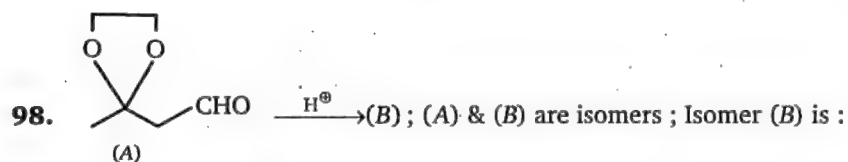
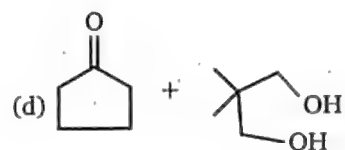
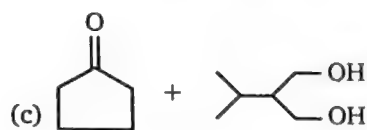
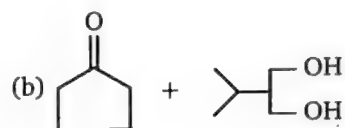
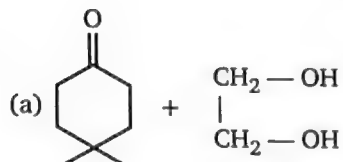
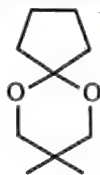
(c) + OH OH (d) + OH OH

98. CHO (A) $\xrightarrow{H^{\oplus}}$ (B) ; (A) & (B) are isomers ; Isomer (B) is :

(a) CH_2 OH (b) O H

(c) O H OH (d) H CH_2 OH

99. OH $\xrightarrow{PCC}$ (A)

OH $\xrightarrow{PCC}$ (B)

(A) and (B) is differentiated by :

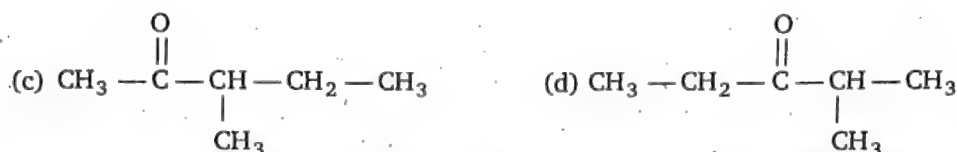
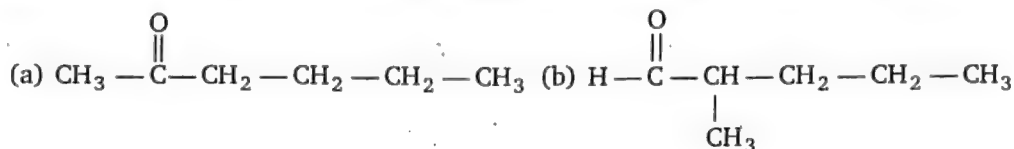
(a) NaH (b) 2-4 DNA (c) Tollen's reagent (d) $NaHSO_3$

100. Which of the following pairs cannot be differentiated by Tollens' reagent ?

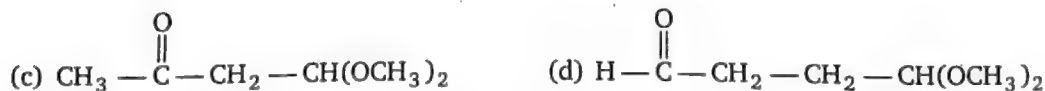
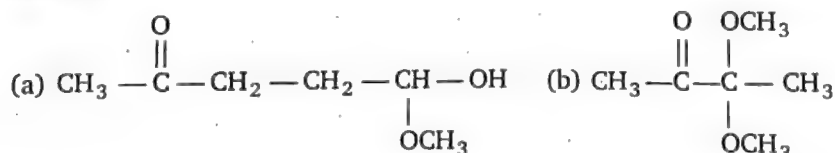
(a) Benzaldehyde and benzyl alcohol (b) Hexanal and 2-hexanone
(c) 2-Hexanol and 2-hexanone (d) Pentanal and diethyl ether

101. An optically active compound $C_6H_{12}O$ gives positive test with 2, 4-dinitrophenyl hydrazine, but negative with Tollens' reagent, what is the structure of the compound ?

(a) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_3$ (b) $H-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3$

(c) $CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$ (d) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$

102. Compound (A) $C_6H_{12}O_3$, when treated with I_2 in aqueous sodium hydroxide gives yellow precipitate. When A is treated with Tollens reagent no reaction occur. When A is hydrolysed and then treated with Tollens reagent, a silver mirror is formed in test tube. Compound (A) will be :

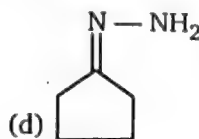
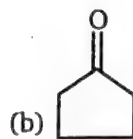
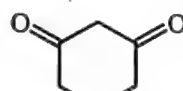
(a) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{OCH_3}{\underset{|}{CH}}-OH$ (b) $CH_3-\overset{O}{\overset{\|}{C}}-\underset{OCH_3}{\underset{|}{\overset{OCH_3}{\overset{|}{C}}}}-CH_3$

(c) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH(OCH_3)_2$ (d) $H-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH(OCH_3)_2$

103. $\begin{array}{l}CH_2-CH_2-CO_2H\\|\\CH_2-CH_2-CO_2H\end{array} \xrightarrow[BaCO_3]{\Delta} A \xrightarrow{NH_2-NH_2} B \xrightarrow[KOH]{heat} (C)$, Product ($C$) obtained is :

(a) $CH_3-CH=CH-CH_2$

(b)

(c)

(d)

104. Which of following does not react with $NaHSO_3$ (sodium bisulphite)?

(a) $CH_3-\overset{O}{\overset{\|}{C}}-H$ (b) $CH_3-\overset{O}{\overset{\|}{C}}-Et$

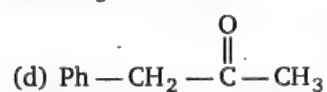
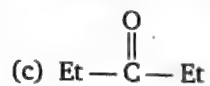
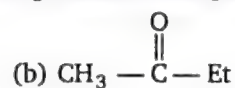
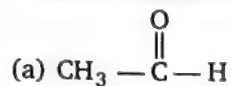
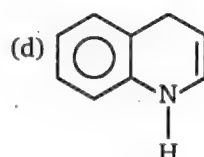
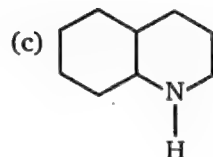
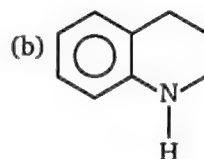
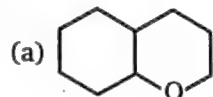
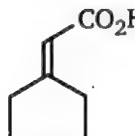
(c) $Et-\overset{O}{\overset{\|}{C}}-Et$ (d) $Ph-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

105. (cyclohexanone bearing $CH_2-CH_2-CH_2-NH_2$ at the 2-position) $\xrightarrow[\text{Raney Ni}]{H_2}$ (A); Product (A) is :

(a) octahydrochromene (fused cyclohexane–tetrahydropyran, O in ring)

(b) 1,2,3,4-tetrahydroquinoline (N–H)

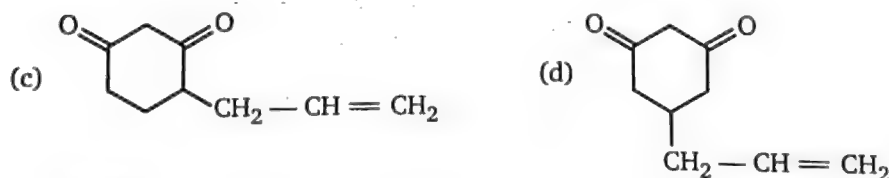
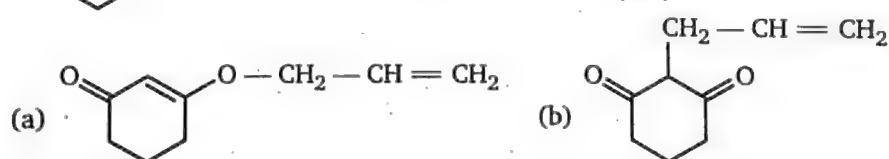
(c) decahydroquinoline (N–H)

(d) 1,4-dihydroquinoline (N–H)

106. (cyclohexane-1,3-dione) $+CH_2=CH-CH_2-Br \xrightarrow[(75\%)]{KOH}$ (A) ; Product (A) is :

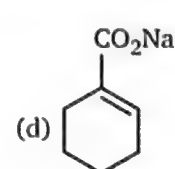
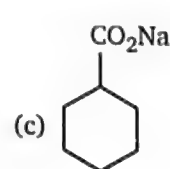
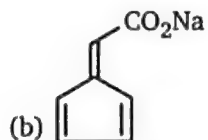
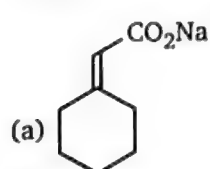
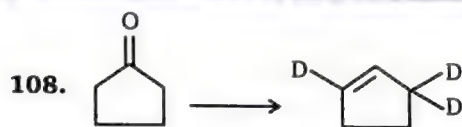
(a) 3-($O-CH_2-CH=CH_2$)cyclohex-2-en-1-one

(b) 2-($CH_2-CH=CH_2$)cyclohexane-1,3-dione

(c) 4-($CH_2-CH=CH_2$)cyclohexane-1,3-dione

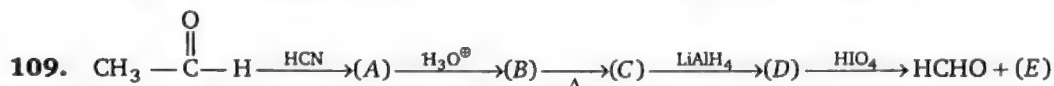
(d) 5-($CH_2-CH=CH_2$)cyclohexane-1,3-dione

107. (cyclohexylidene acetic acid, $=CH-CO_2H$) $\xrightarrow[(2)\,HCl/H_2O]{(1)\,Me\text{-}Li(excess)}$ (A) $\xrightarrow[NaOH]{I_2}$ $(B)+CHI_3$; Product (B) in this reaction is :

(a) cyclohexylidene–$CH-CO_2Na$ (b) cyclopentadienylidene–$CH-CO_2Na$ (c) cyclohexyl–CO_2Na (d) cyclohex-1-enyl–CO_2Na

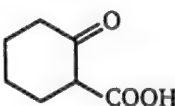
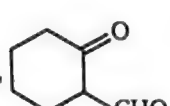
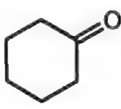
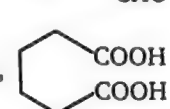
108. Cyclopentanone ⟶ 1,3,3-trideuterio-cyclopentene (D on ring)

Arrange the following reagent in the correct order in which above transformation is carried out :

(a) $KOD/D_2O, H^+/\Delta, LiAlH_4$ (b) $H^+/\Delta, KOD/D_2O, LiAlH_4$

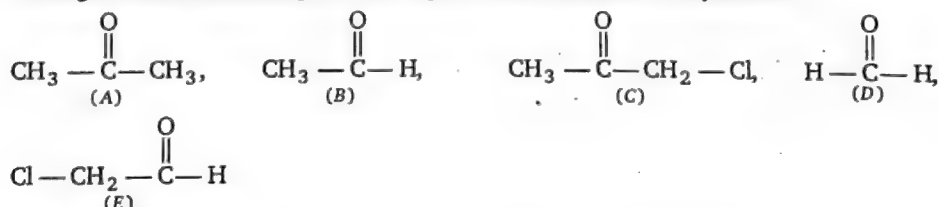
(c) $KOD/D_2O, LiAlH_4, H^+/\Delta$ (d) $LiAlH_4, H^+/\Delta, KOD/D_2O$

109. $CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{HCN} (A) \xrightarrow{H_3O^{\oplus}} (B) \xrightarrow[\Delta]{} (C) \xrightarrow{LiAlH_4} (D) \xrightarrow{HIO_4} HCHO + (E)$

Compound (*C*) can show geometrical isomerism. Product (*E*) of the reaction will be :

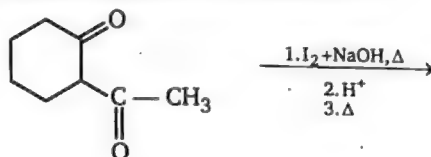
(a) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (b) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$

(c) CH_3-CHO (d) $HCHO$

110. Arrange in their increasing order of equilibrium constants for hydration ?

$\underset{(A)}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$, $\underset{(B)}{CH_3-\overset{O}{\overset{\|}{C}}-H}$, $\underset{(C)}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-Cl}$, $\underset{(D)}{H-\overset{O}{\overset{\|}{C}}-H}$,

$\underset{(E)}{Cl-CH_2-\overset{O}{\overset{\|}{C}}-H}$

(a) $A < B < C < D < E$ (b) $A < C < B < E < D$

(c) $A < C < E < B < D$ (d) $C < A < B < E < D$

111. End products of the following sequence of reactions are :

2-acetylcyclohexanone (C_6 ring with C=O and $-\overset{O}{\overset{\|}{C}}-CH_3$) $\xrightarrow[\text{2. } H^+ \text{ 3. } \Delta]{\text{1. } I_2 + NaOH, \Delta}$

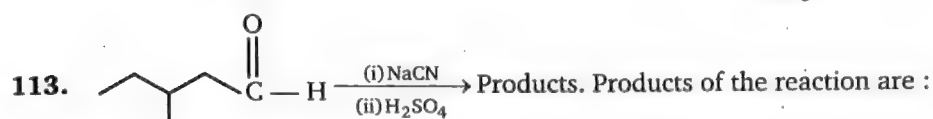
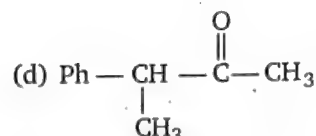
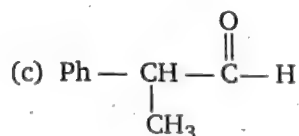
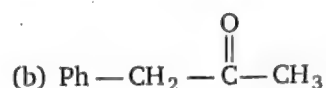
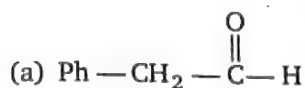
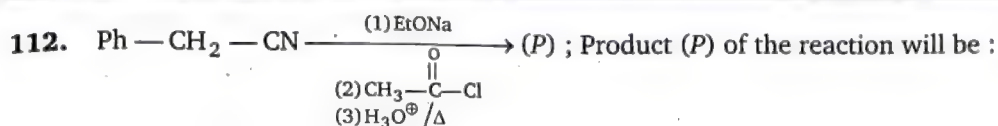
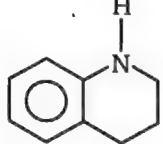
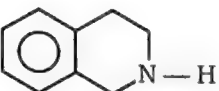
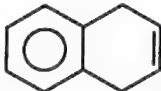
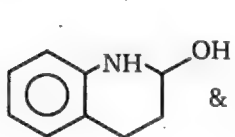
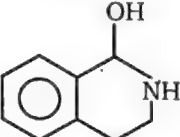
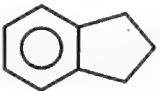
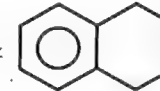
(a) yellow ppt. of CHI_3, 2-oxocyclohexane-COOH (b) yellow ppt. of CHI_3, 2-oxocyclohexane-CHO

(c) yellow ppt. of CHI_3, cyclohexanone (d) yellow ppt. of CHI_3, ring with COOH, COOH

112. $Ph-CH_2-CN \xrightarrow[(2)\,CH_3-\overset{O}{\overset{||}{C}}-Cl \quad (3)\,H_3O^{\oplus}/\Delta]{(1)\,EtONa} (P)$; Product (*P*) of the reaction will be :

(a) $Ph-CH_2-\overset{O}{\overset{||}{C}}-H$ (b) $Ph-CH_2-\overset{O}{\overset{||}{C}}-CH_3$

(c) $Ph-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-H$ (d) $Ph-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-CH_3$

113. (skeletal structure: branched alkyl chain)$-\overset{O}{\overset{||}{C}}-H \xrightarrow[(ii)\,H_2SO_4]{(i)\,NaCN}$ Products. Products of the reaction are :

(a) Racemic mixture
(b) Diastereomers
(c) Meso
(d) Mixture of meso compound and optically active compound

114. $(A) \xrightarrow[\text{dil. } H_2SO_4]{HgSO_4} (B) \xrightarrow{LiAlH_4} \underset{\text{recemic mixture}}{(C)}$

∴ reactant (*A*) is :

(a) $CH_3-C\equiv CH$ (b) $HC\equiv CH$
(c) $CH_3-C\equiv C-CH_3$ (d) $Ph-CH=CH_2$

115. $CH_3CH_2-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow[HCl]{NaNO_2}$; Major product of this reaction is :

(a) $CH_3\underset{NO}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-CH_3$ (b) $CH_3-CH_2-\overset{O}{\overset{||}{C}}-CH=N-OH$

(c) $CH_3-\underset{N-OH}{\underset{||}{C}}-\overset{O}{\overset{||}{C}}-CH_3$ (d) $CH_3-CH_2-\underset{N-OH}{\underset{||}{C}}-CH_3$

116. (1) NH_2OH (2) H^+, Δ (3) $LiAlH_4$ → (A) + (B). Product (A) & (B) are :

(a) H, N, & N—H (b) & (c) NH, OH & OH, NH (d) &

O, CH

117. 3, 4-Methylene dioxybenzaldehyde + CH_3NO_2 (nitromethane) $\xrightarrow{NaOH}$ A $\xrightarrow[\Delta]{HCl}$ (B). 93% Product (B) is :

(a) HO, OH, $CH = CH — NO_2$

(b) O, O, $CH{=}CH — NO_2$

(c) HO, $CH = CH — NO_2$

(d) O, O, OH, $CH — CH_2 — NO_2$

118. O, (1) HCN (2) $LiAlH_4$ (3) $NaNO_2/H^+$ → (A) major. Product (A) is :

(a) O (b) O (c) (d)

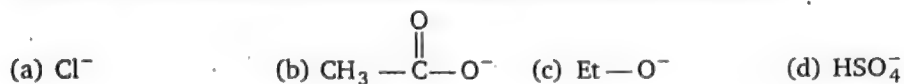
119. Cl–CH₂CH₂CH₂–CO–CH₂CH₂CH₂–Cl $\xrightarrow[\text{(2mole)}]{\text{alc. KOH}}$ (A). Product (A) is :

(a) $CH_2=CH-CH_2-CO-CH_2-CH=CH_2$ (b) cyclopropyl–C(=O)–cyclopropyl

(c) $CH_3-CH=CH-CO-CH=CH-CH_3$ (d) $HO-CH_2CH_2CH_2-CO-CH_2CH_2CH_2-OH$

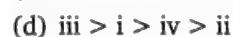
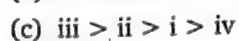
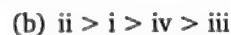
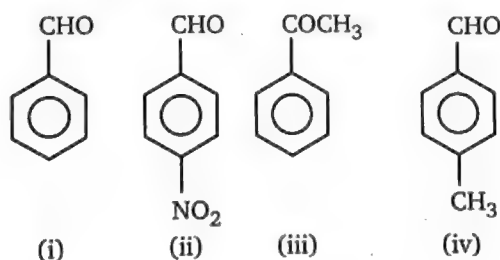
120. $R-\overset{O}{\overset{\|}{C}}-R \underset{\text{(catalyst)}}{\overset{\text{HCN}}{\rightleftharpoons}} R-\underset{CN}{\overset{OH}{C}}-R$

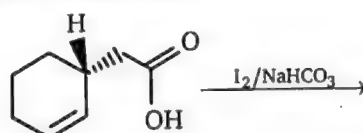
Which of following can be used as a catalyst in the above reaction?

(a) Cl^- (b) $CH_3-\overset{O}{\overset{\|}{C}}-O^-$ (c) $Et-O^-$ (d) HSO_4^-

121. Arrange the following carbonyl compounds in decreasing order of their reactivity in nucleophilic addition reaciton.

(i) C_6H_5CHO (ii) $p\text{-}NO_2C_6H_4CHO$ (iii) $C_6H_5COCH_3$ (iv) $p\text{-}CH_3C_6H_4CHO$

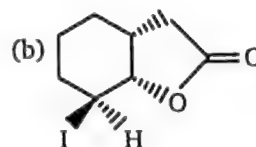
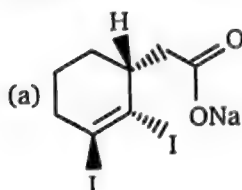
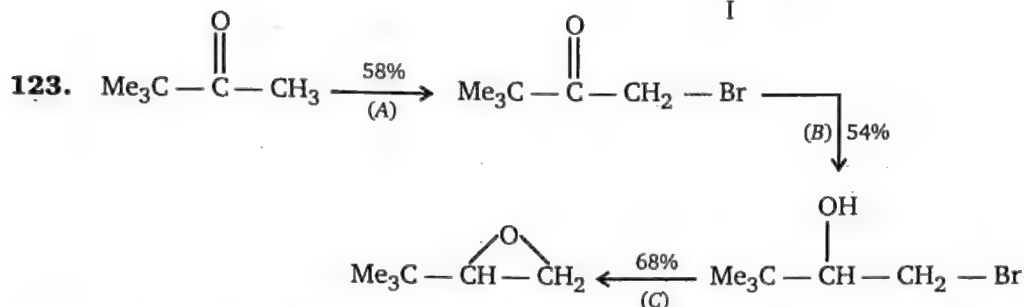
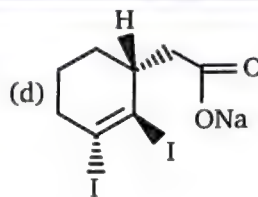
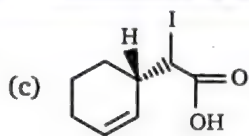
(a) ii > iii > i > iv (b) ii > i > iv > iii

(c) iii > ii > i > iv (d) iii > i > iv > ii

122. The following reaction were carried out.

(cyclohex-2-enyl)acetic acid (H wedge, CH_2COOH) $\xrightarrow{I_2/NaHCO_3}$

The final product formed in the above reaction sequence is :

(a) sodium (diiodocyclohexyl)acetate (H, I, I, ONa) (b) iodo bicyclic lactone (I, H, O, =O)

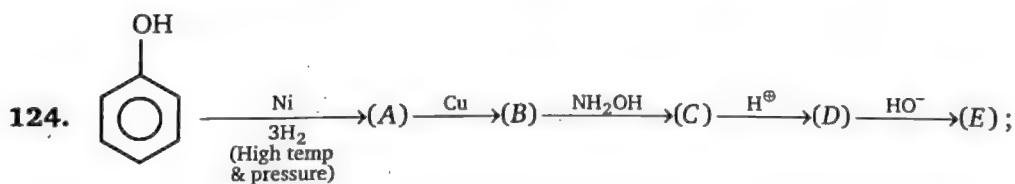
(c) [structure] (d) [structure]

123. $Me_3C-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow[(A)]{58\%} Me_3C-\overset{O}{\overset{||}{C}}-CH_2-Br \xrightarrow[(B)]{54\%} Me_3C-\overset{OH}{\overset{|}{C}H}-CH_2-Br \xrightarrow[(C)]{68\%} Me_3C-\overset{O}{CH-CH_2}$

A. Yield of each step as actually carried out in the laboratory is given above. What is overall yield of reaction?

(a) 42% (b) 31%
(c) 21% (d) 60%

B. What is the appropriate reagent to carry out above synthesis, *i.e.*, *A*, *B*, *C* respectively are :

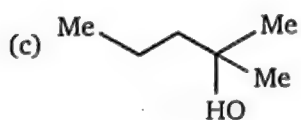
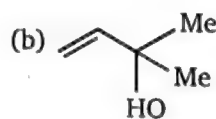
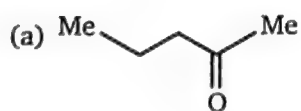
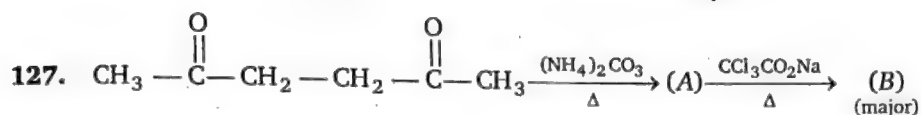
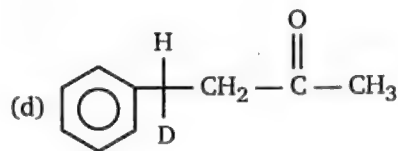
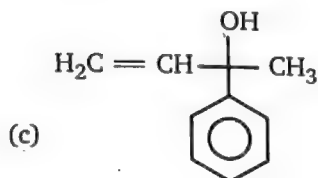
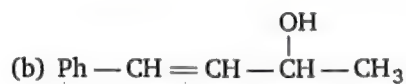
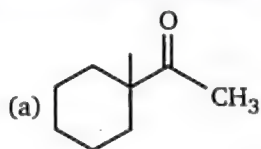
(a) Br_2/H^+, $LiAlH_4, H^{\oplus}$ (b) $Br_2/H^+, NaBH_4, HO^-$
(c) NBS, $AlCl_3, HO^-$ (d) $Br_2/HO^-, BF_3, HO^-$

124. Phenol $\xrightarrow[\text{3H}_2 \text{ (High temp \& pressure)}]{\text{Ni}} (A) \xrightarrow{\text{Cu}} (B) \xrightarrow{NH_2OH} (C) \xrightarrow{H^{\oplus}} (D) \xrightarrow{HO^-} (E)$;

Product (*E*) is :

(a) Nylon 66 (b) Nylon 6 (c) Styrene (d) Polystyrene

125. Methyl vinyl ketone on reaction with $LiCuMe_2$ gives a major product, whose structure is :

(a) [structure: Me–CH₂–CH₂–C(=O)–Me] (b) [structure: CH₂=CH–C(OH)(Me)Me]

(c) [structure: Me–CH₂–CH₂–C(OH)(Me)Me] (d) [structure: cyclopropyl methyl ketone]

126. Which of following is in capable to show iodoform test ?

(a) Cyclohexyl–C(=O)–CH_3 (O, CH_3)

(b) $Ph—CH=CH—\overset{OH}{CH}—CH_3$

(c) $H_2C=CH—C(OH)(C_6H_5)—CH_3$ (OH, CH_3)

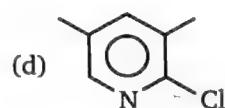
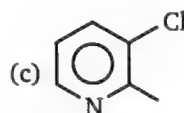
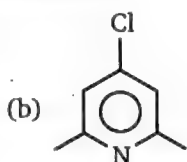
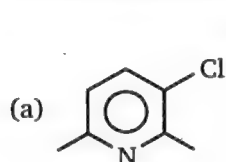
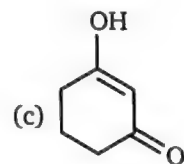
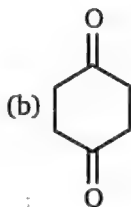
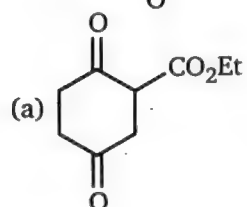
(d) $C_6H_5—C(H)(D)—CH_2—\overset{O}{\overset{||}{C}}—CH_3$

127. $CH_3—\overset{O}{\overset{||}{C}}—CH_2—CH_2—\overset{O}{\overset{||}{C}}—CH_3 \xrightarrow[\Delta]{(NH_4)_2CO_3} (A) \xrightarrow[\Delta]{CCl_3CO_2Na} \underset{\text{(major)}}{(B)}$

Product (*B*) of above reaction is :

(a) Cl, N (b) Cl, N (c) Cl, N (d) N, Cl

128. EtO_2C, CO_2Et, O, O $\xrightarrow[\Delta]{H_3O^+} A$; Product obtained is :

(a) O, CO_2Et, O (b) O, O (c) OH, O (d) None of these

129. $\underset{\substack{\text{Symmetrical}\\\text{Ketone}}}{(A)} \xrightarrow{LiAlH_4} (B) \xrightarrow[\Delta]{H^{\oplus}}$ Diastereomers

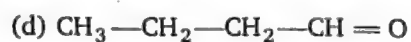
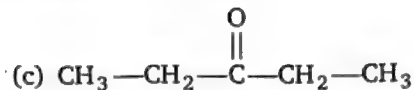
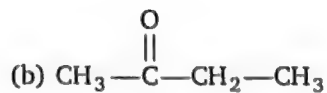
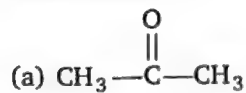
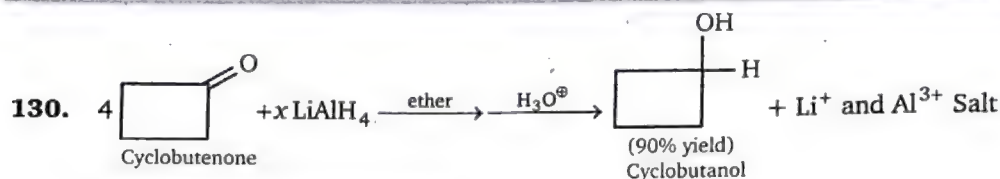
Reactent (*A*) is :

(a) $CH_3—\overset{O}{\overset{||}{C}}—CH_3$

(b) $CH_3—\overset{O}{\overset{||}{C}}—CH_2—CH_3$

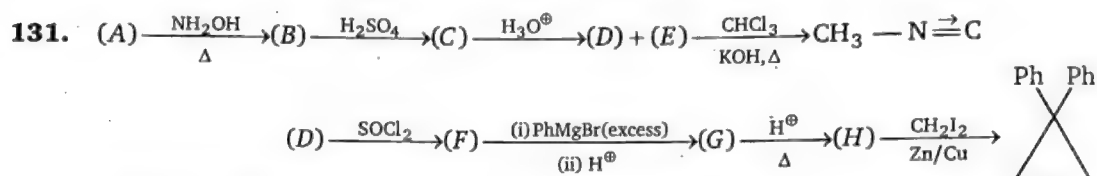
(c) $CH_3—CH_2—\overset{O}{\overset{||}{C}}—CH_2—CH_3$

(d) $CH_3—CH_2—CH_2—CH=O$

130. 4 [Cyclobutenone] $+ x\,LiAlH_4 \xrightarrow{ether} \xrightarrow{H_3O^{\oplus}}$ [Cyclobutanol, OH, H] (90% yield) $+ Li^+$ and Al^{3+} Salt

Value of x in above reaction is :

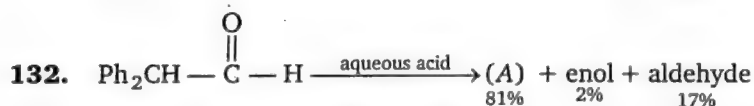
(a) 1 (b) 2 (c) 3 (d) 4

131. $(A) \xrightarrow[\Delta]{NH_2OH} (B) \xrightarrow{H_2SO_4} (C) \xrightarrow{H_3O^{\oplus}} (D) + (E) \xrightarrow[KOH,\Delta]{CHCl_3} CH_3-N \rightleftarrows C$

$(D) \xrightarrow{SOCl_2} (F) \xrightarrow[\text{(ii) } H^{\oplus}]{\text{(i) PhMgBr(excess)}} (G) \xrightarrow[\Delta]{H^{\oplus}} (H) \xrightarrow[Zn/Cu]{CH_2I_2}$ [cyclopropane with Ph, Ph]

Molecular weight of compound (A) is :

(a) 58 (b) 120

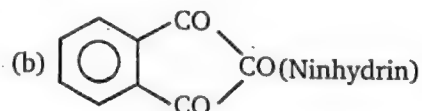
(c) 60 (d) 182

132. $Ph_2CH-\overset{O}{\overset{||}{C}}-H \xrightarrow{\text{aqueous acid}} \underset{81\%}{(A)} + \underset{2\%}{\text{enol}} + \underset{17\%}{\text{aldehyde}}$

Product (A) of above reaction will be :

(a) $Ph-\underset{Ph}{\underset{|}{C}}=CH-O$ (b) $Ph_2CH-\overset{OH}{\overset{|}{CH_2}}$

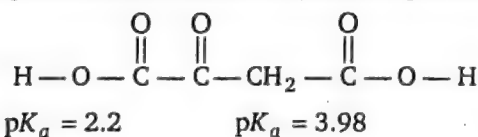
(c) $Ph_2CH-\overset{OH}{\overset{|}{CH}}-OH$ (d) $Ph_2CH-\overset{O}{\overset{||}{C}}-CH_3$

133. Which of the following will form stable hydrate ?

(a) CCl_3CHO (Chloral) (b) [benzene ring fused with CO, CO, CO] (Ninhydrin)

(c) $(CF_3)_2CO$ (d) All of these

134. The pH at which maximum hydrate is present in an solution of oxaloacetic acid:

$H-O-\overset{O}{\overset{||}{C}}-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-O-H$

$pK_a = 2.2$ $pK_a = 3.98$

(a) pH = 0 (b) pH = 12

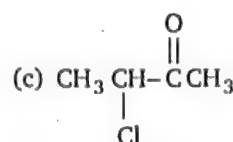
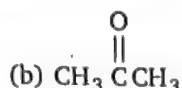
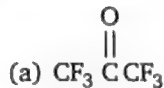
(c) pH = 4 (d) pH = 6

135. Arrange their stabilities of given gem- diols in decreasing order.

(I)   (II) (III)

(a) I > II > III (b) III > II > I (c) I > III > II (d) III > I > II

136. Maximum hydration takes place of :

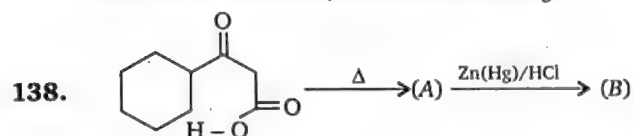
(a) $CF_3\overset{O}{\overset{\|}{C}}CF_3$ (b) $CH_3\overset{O}{\overset{\|}{C}}CH_3$ (c) $CH_3\underset{Cl}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}CH_3$ (d) $C_6H_5\overset{O}{\overset{\|}{C}}C_6H_5$

137. The conversion, $PhCN \rightarrow PhCOCH_3$, can be achieved most conveniently by reaction with:

(a) CH_3MgBr followed by hydrolysis

(b) I_2 — NaOH, CH_3I

(c) dil. H_2SO_4 followed by reaction with CH_2N_2

(d) LAH followed by reaction with CH_3I

138.

In the above reaction, product (*B*) is:

(a) (b)

(c) (d) OH

139. $(A) \xrightarrow{LiAlH_4} (B) \xrightarrow[\Delta]{H^{\oplus}}$

Structure of *A* is :

(a)   (b)   (c)   (d)

140. (methylene-oxetanone) $\xrightarrow{O_3}$ HCHO + (A) $\xrightarrow{Ph-NH_2}$ (B)

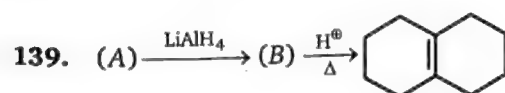
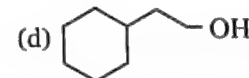
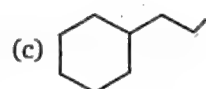
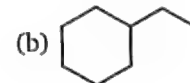
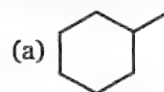
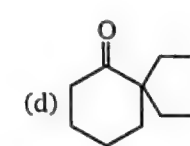
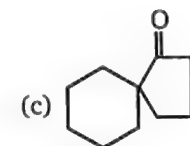
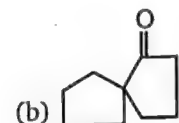
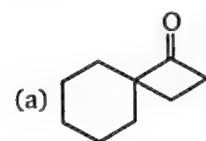
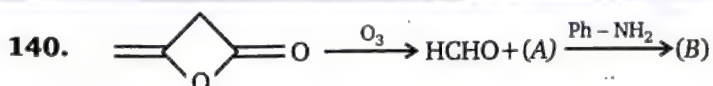
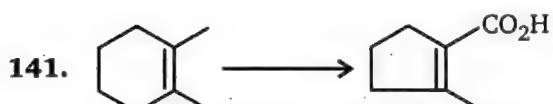
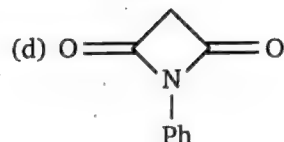
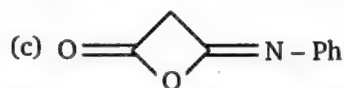
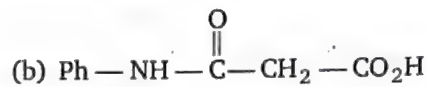
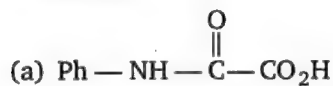
Product (B) is :

(a) $Ph-NH-\overset{O}{\overset{||}{C}}-CO_2H$

(b) $Ph-NH-\overset{O}{\overset{||}{C}}-CH_2-CO_2H$

(c) O=(oxetane ring)=N – Ph

(d) O=(azetidine ring, N–Ph)=O

141. (1,2-dimethylcyclohexene) ⟶ (2-methylcyclopent-1-ene carboxylic acid, CO_2H)

To carry out above conversion, arrange the following reagents in correct order.

O_3/Zn (1) EtONa / EtOH/Δ (2) NaOCl (3) H^+ (4)

(a) 1 → 3 → 2 → 4
(b) 1 → 2 → 4 → 3
(c) 1 → 3 → 4 → 2
(d) 1 → 2 → 3 → 4

142. $H_2C=CH-CH_2-CH_2-\underset{CH_2-CH_3}{\overset{HOCH_2}{C}}-OH \xrightarrow[TsOH]{CH_3-\overset{O}{\overset{||}{C}}-CH_3} (A) \xrightarrow[(CH_3)_2S]{O_3} (B) + HCHO$

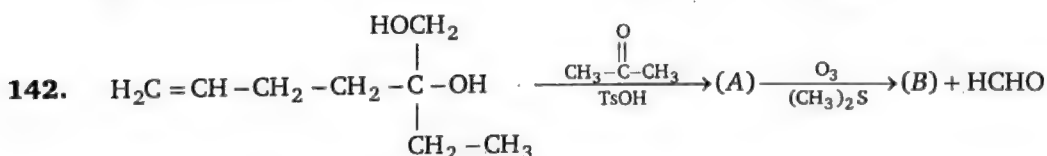
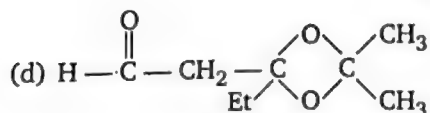
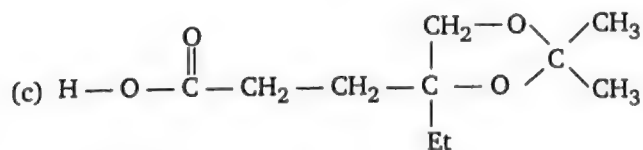
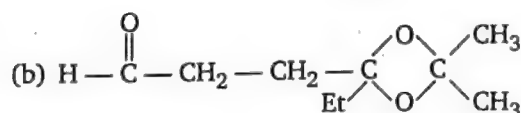
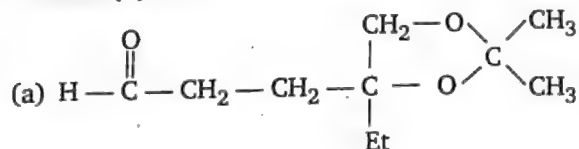
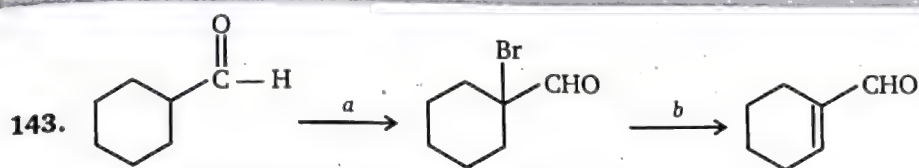
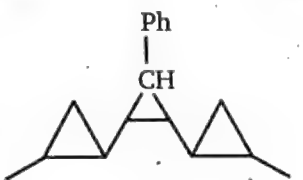
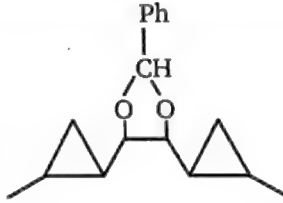
Product (B) is:

(a) $H-\overset{O}{\overset{||}{C}}-CH_2-CH_2-\underset{Et}{\overset{CH_2-O}{C}}-O$ (ring closed through $C(CH_3)_2$)

(b) $H-\overset{O}{\overset{||}{C}}-CH_2-CH_2-C(Et)$ (ring –O–$C(CH_3)_2$–O–)

(c) $H-O-\overset{O}{\overset{||}{C}}-CH_2-CH_2-\underset{Et}{\overset{CH_2-O}{C}}-O$ (ring closed through $C(CH_3)_2$)

(d) $H-\overset{O}{\overset{||}{C}}-CH_2-C(Et)$ (ring –O–$C(CH_3)_2$–O–)

143. Cyclohexyl–C(=O)–H $\xrightarrow{a}$ 1-bromocyclohexane-CHO $\xrightarrow{b}$ cyclohex-1-ene-CHO

Identify appropriate reagents for the above reaction:

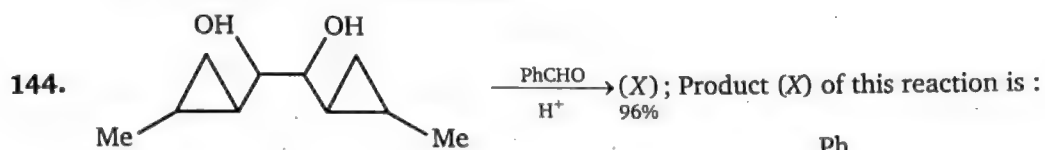
(a) $a = Br_2/CCl_4$, $b =$ aq. KOH

(b) $a = Br_2/H^+$, $b =$ aq. KOH

(c) $a = Br_2/H^+$, $b =$ alc. KOH

(d) $a = Br_2/HO^-$, $b =$ aq. KOH

144.

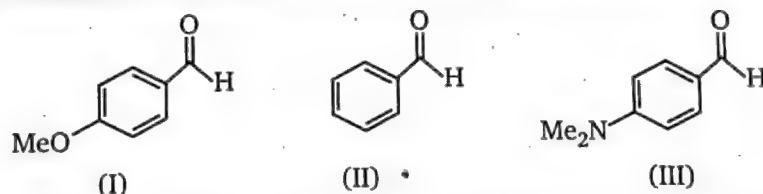
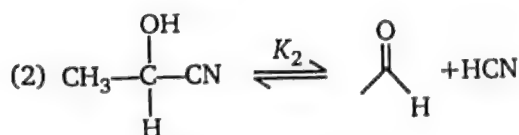
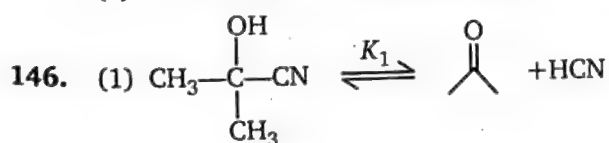
$\xrightarrow[H^+]{PhCHO}$ (X); Product (X) of this reaction is : 96%

(a) (b) (c) (d)

145. The $K_{eq.}$ values in HCN addition to following aldehydes are in the order :

MeO–C_6H_4–CHO (I) C_6H_5–CHO (II) Me_2N–C_6H_4–CHO (III)

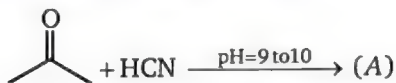
(a) I > II > III (b) II > III > I (c) III > I > II (d) II > I > III

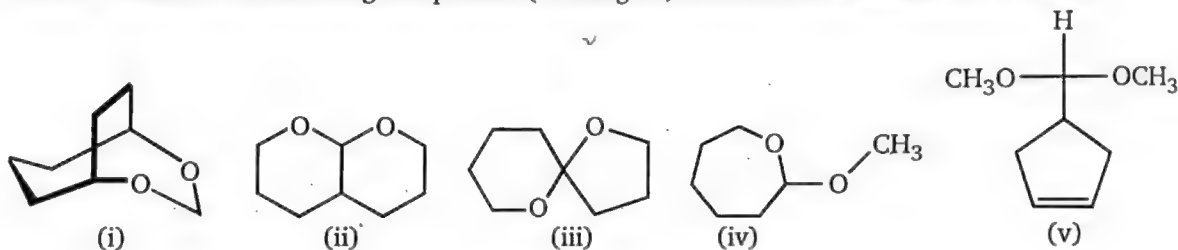
146. (1) $CH_3-C(OH)(CH_3)-CN \overset{K_1}{\rightleftharpoons}$ $(CH_3)_2C=O$ + HCN

(2) $CH_3-C(OH)(H)-CN \overset{K_2}{\rightleftharpoons}$ CH_3CHO + HCN

elation between K_1 and K_2 is :

(a) $K_1 = K_2$ (b) $K_1 > K_2$ (c) $K_2 > K_1$ (d) $K_1 = K_2 = 1$

147. Which of the following is correct for the reaction ?

$$CH_3COCH_3 + HCN \xrightarrow{pH=9\,to\,10} (A)$$

(a) A is cyanohydrin
(b) Nucleophilic-addition reaction
(c) The above reaction is not shown by alkenes
(d) All of these

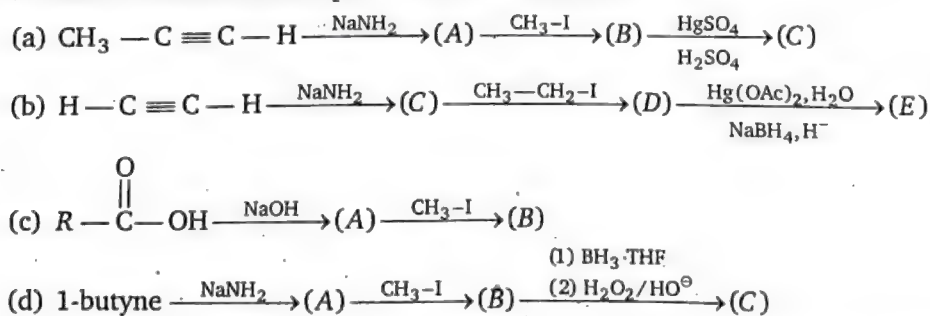
148. Which of the following compounds (i through v) should not be classified as an acetal ?

(a) ii and iii
(b) iv
(c) i
(d) none (they are all acetals)

149. In which of reactions final product is NOT a ketone :

(a) $CH_3-C\equiv C-H \xrightarrow{NaNH_2} (A) \xrightarrow{CH_3-I} (B) \xrightarrow[H_2SO_4]{HgSO_4} (C)$

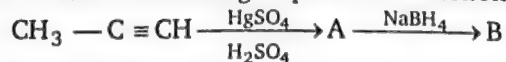
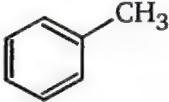
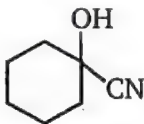
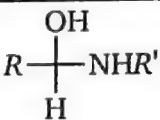
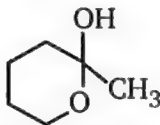
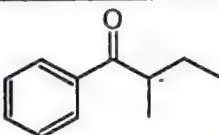
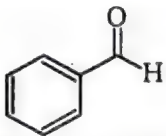
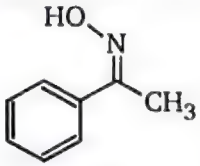
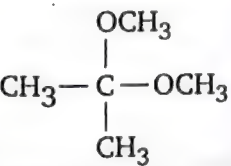
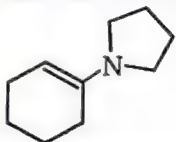
(b) $H-C\equiv C-H \xrightarrow{NaNH_2} (C) \xrightarrow{CH_3-CH_2-I} (D) \xrightarrow[NaBH_4, H^-]{Hg(OAc)_2, H_2O} (E)$

(c) $R-\overset{O}{\overset{||}{C}}-OH \xrightarrow{NaOH} (A) \xrightarrow{CH_3-I} (B)$

(d) 1-butyne $\xrightarrow{NaNH_2} (A) \xrightarrow{CH_3-I} (B) \xrightarrow[(2)\ H_2O_2/HO^{\ominus}]{(1)\ BH_3\cdot THF} (C)$

150. The reaction of ethyl methyl ketone with Cl_2/excess OH^- gives the following major product

(a) $ClCH_2CH_2COCH_3$
(b) $CH_3CH_2COCCl_3$
(c) $ClCH_2CH_2COCH_2Cl$
(d) $CH_3CCl_2COCH_2Cl$

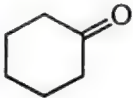
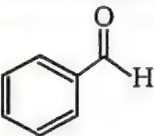
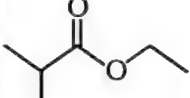
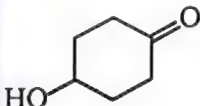
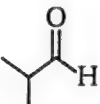
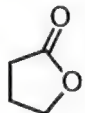
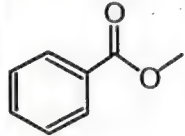
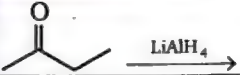
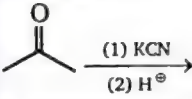
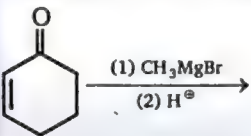
151. The product obtained from the following sequence of reactions is

$$CH_3-C\equiv CH \xrightarrow[H_2SO_4]{HgSO_4} A \xrightarrow{NaBH_4} B$$

(a) propanol
(b) 2-propanol
(c) 1-propanol
(d) propanhe

ANSWERS — LEVEL 1

1.	(a)	**2.**	(b)	**3.**	(d)	**4.**	(c)	**5.**	(a)	**6.**	(c)	**7.**	(b)	**8.**	(b)
9.	(b)	**10.**	(c)	**11.**	(c)	**12.**	(c)	**13.**	(b)	**14.**	(b)	**15.**	(b)	**16.**	(b)
17.	(b)	**18.**	(b)	**19.**	(b)	**20.**	(d)	**21.**	(b)	**22.**	(b)	**23.**	(b)	**24.**	(d)
25.	(c)	**26.**	(b)	**27.**	(b)	**28.**	(a)	**29.**	(b)	**30.**	(c)	**31.**	(d)	**32.**	(c)
33.	(b)	**34.**	(b)	**35.**	(a)	**36.**	(b)	**37.**	(c)	**38.**	(d)	**39.**	(b)	**40.**	(a)
41.	(b)	**42.**	(a)	**43.**	(a)	**44.**	(b)	**45.**	(b)	**46.**	(a)	**47.**	(b)	**48.**	(d)
49.	(c)	**50.**	(b)	**51.**	(d)	**52.**	(b)	**53.**	(b)	**54.**	(c)	**55.**	(b)	**56.**	(b)
57.	(a)	**58.**	(d)	**59.**	(c)	**60.**	(c)	**61.**	(c)	**62.**	(a)	**63.**	(b)	**64.**	(b)
65.	(b)	**66.**	(d)	**67.**	(b)	**68.**	(d)	**69.**	(b)	**70.**	(c)	**71.**	(b)	**72.**	(d)
73.	(d)	**74.**	(a)	**75.**	(d)	**76.**	(a)	**77.**	(a)	**78.**	(a)	**79.**	(c)	**80.**	(c)
81.	(d)	**82.**	(b)	**83.**	(b)	**84.**	(b)	**85.**	(b)	**86.**	(a)	**87.**	(b)	**88.**	(c)
89.	(b)	**90.**	(b)	**91.**	(c)	**92.**	(b)	**93.**	(b)	**94.**	(b)	**95.**	(c)	**96.**	(c)
97.	(d)	**98.**	(b)	**99.**	(c)	**100.**	(c)	**101.**	(c)	**102.**	(c)	**103.**	(c)	**104.**	(c)
105.	(c)	**106.**	(b)	**107.**	(a)	**108.**	(c)	**109.**	(c)	**110.**	(b)	**111.**	(c)	**112.**	(b)
113.	(b)	**114.**	(c)	**115.**	(c)	**116.**	(a)	**117.**	(a)	**118.**	(a)	**119.**	(b)	**120.**	(c)
121.	(b)	**122.**	(b)	**123.**	A-c	**123.**	B-b	**124.**	(b)	**125.**	(a)	**126.**	(c)	**127.**	(a)
128.	(b)	**129.**	(c)	**130.**	(a)	**131.**	(a)	**132.**	(c)	**133.**	(d)	**134.**	(a)	**135.**	(a)
136.	(a)	**137.**	(a)	**138.**	(b)	**139.**	(d)	**140.**	(b)	**141.**	(d)	**142.**	(a)	**143.**	(c)
144.	(b)	**145.**	(d)	**146.**	(b)	**147.**	(d)	**148.**	(d)	**149.**	(c)	**150.**	(b)	**151.**	(b)

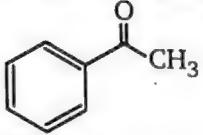
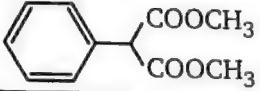
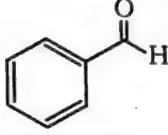
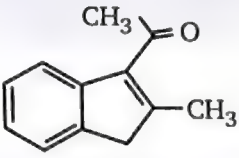
LEVEL-2

1. Select the best choice for example (A to L) from the examples (a to n) given below. Write your choice in the box given.

A.	An acetal derivative of a ketone.	
B.	A chiral ketone.	
C.	An aldehyde that gives a aldol condensation with itself.	
D.	An oxime derivative	
E.	A reagent that reduces aldehydes to 1°- alcohols.	
F.	An α, β-unsaturated ketone.	
G.	A reagent that oxidizes aldehydes to carboxylic acids.	
H.	A reagent that reduces ketones to alkanes.	
I.	An enamine derivative of a ketone.	
J.	An intermediate in imine formation.	
K.	A cyclic hemiacetal.	
L.	A cyanohydrin derivative.	

(a)	CH_3	**(b)**	OH, CN	**(c)**	O
(d)	OH R—C—NHR' H	**(e)**	OH, O, CH_3	**(f)**	$Zn(Hg)H_3O^{(+)}$
(g)	O	**(h)**	$NaBH_4$ aq. alcohol	**(i)**	O, H
(j)	$Ag(NH_3)_2^{(+)}OH^{(-)}$	**(k)**	HO, N, CH_3	**(l)**	OCH_3 $CH_3-C-OCH_3$ CH_3

2. The following questions refer to the compounds (A to G) shown below :

i.	Which compounds are reduced by sodium borohydride ?	ii.	Which compounds are hydrolyzed by hot aqueous acid ?	iii.	Which compound are oxidisized by CrO_3/pyridine?

A		E			A		E			A		E	
B		F			B		F			B		F	
C		G			C		G			C		G	
D		H			D		H			D		H	

A.		B.	H	C.		D.	O
E.	HO	F.	H	G.	O	H.	O

3. **Match the column:**

	Column (I)		Column (II)
(a)	$\xrightarrow{LiAlH_4}$	(p)	racemic mixture
(b)	$\xrightarrow[(2)\ H^{\oplus}]{(1)\ KCN}$	(q)	Diastereomers
(c)	$Ph—CH_2—Cl \xrightarrow{KCN}$	(r)	Nu-addition reaction
(d)	$\xrightarrow[(2)\ H^{\oplus}]{(1)\ CH_3MgBr}$	(s)	Nu-Substitutions reaction

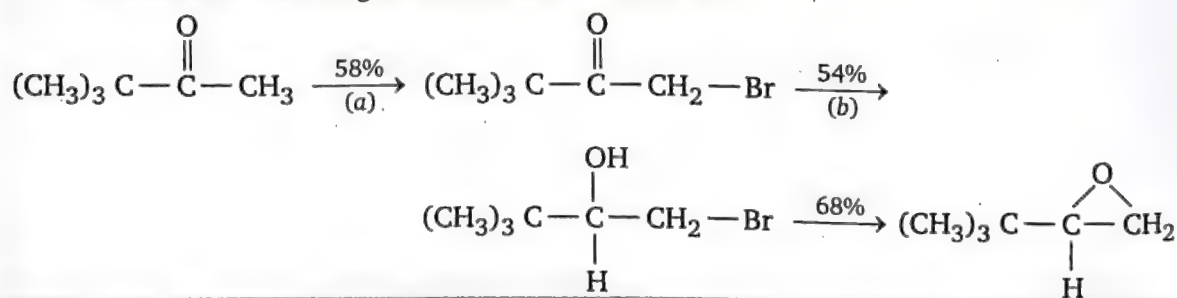
4. Complete the following table.

	REACTANT	REAGENT(S)/ CONDITIONS	MAJOR ORGANIC PRODUCTS
a.	$C_6H_5-CO-CH_3$	$H_2/Pd-C$ in ethanol (solvent)	A
b.	$C_6H_5-CH(COOCH_3)_2$	$H^+/H_2O/\Delta$	B
c.	C_6H_5-CHO	$(CH_3)_2\overset{-}{C}-\overset{+}{P}(C_6H_5)_3$	C
d.	cyclopent-2-en-1-one	1. $Li^+[(CH_3)_2Cu]^-$ in dry ether 2. H^+/H_2O	D
e.	E	OH^-/ethanol/Δ	indene bearing $-COCH_3$ and $-CH_3$ (CH$_3$, =O, CH$_3$)

5. Comprehension

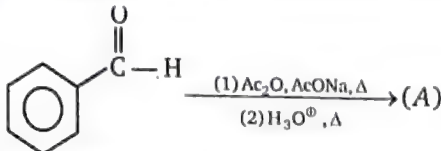
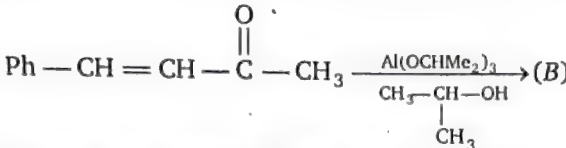
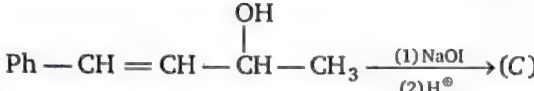
Consider the following reactions and answer A and B.

$$(CH_3)_3C-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[(a)]{58\%} (CH_3)_3C-\overset{O}{\overset{\|}{C}}-CH_2-Br \xrightarrow[(b)]{54\%}$$

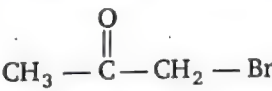
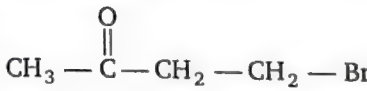
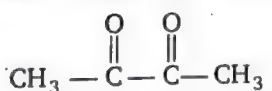
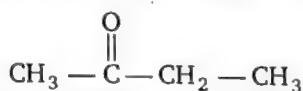
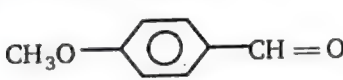
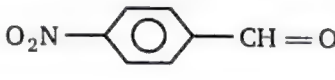
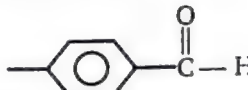
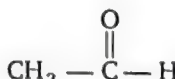
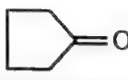
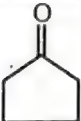
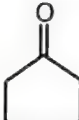
$$(CH_3)_3C-\underset{H}{\overset{OH}{C}}-CH_2-Br \xrightarrow{68\%} (CH_3)_3C-\underset{H}{C}\overset{O}{\frown}CH_2$$

A. Suggest a reagent appropriate step (*a*) the synthesis.

(a) HO^-/Br_2 (1 mole) (b) H^+/Br_2 (1 mole)

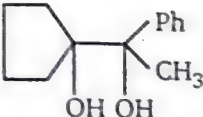
(c) both (a) and (b) (d) None of these

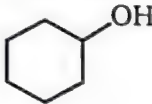
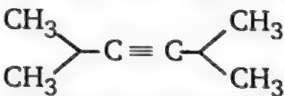
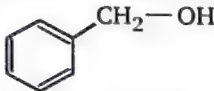
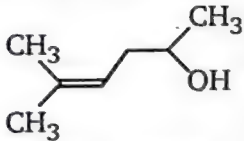
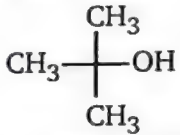
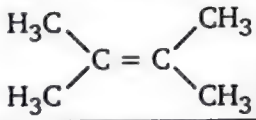
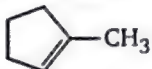
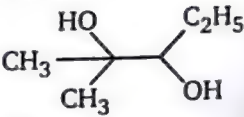
B. Yield of each step as actually carried out in laboratory is given above each arrow. What is overall yield of the reaction ?

(a) 60% (b) 21% (c) 40% (d) 68%

6.

Reaction 1.	$C_6H_5-\overset{O}{\overset{\Vert}{C}}-H \xrightarrow[(2)\,H_3O^{\oplus},\,\Delta]{(1)\,Ac_2O,\,AcONa,\,\Delta} (A)$
Reaction 2.	$Ph-CH=CH-\overset{O}{\overset{\Vert}{C}}-CH_3 \xrightarrow[CH_3-CH(CH_3)-OH]{Al(OCHMe_2)_3} (B)$
Reaction 3.	$Ph-CH=CH-\underset{}{\overset{OH}{\overset{\vert}{CH}}}-CH_3 \xrightarrow[(2)\,H^{\oplus}]{(1)\,NaOI} (C)$

Degree of unsaturation present in compound (*A* + *B* + *C*) is ?

7. Within each set, which compound should be more reactive toward carbonyl addition reaction ?

	A	B
Set (1)	$CH_3-\overset{O}{\overset{\Vert}{C}}-CH_2-Br$	$CH_3-\overset{O}{\overset{\Vert}{C}}-CH_2-CH_2-Br$
Set (2)	$CH_3-\overset{O}{\overset{\Vert}{C}}-\overset{O}{\overset{\Vert}{C}}-CH_3$	$CH_3-\overset{O}{\overset{\Vert}{C}}-CH_2-CH_3$
Set (3)	$CH_3O-C_6H_4-CH=O$	$O_2N-C_6H_4-CH=O$
Set (4)	$CH_3-C_6H_4-\overset{O}{\overset{\Vert}{C}}-H$	$CH_3-\overset{O}{\overset{\Vert}{C}}-H$
Set (5)	cyclopropanone (▷=O)	cyclopentanone (⬠=O)

Set (6)	(tetrahydroquinoline with CHO; N–H)	(tetrahydroquinoline with CHO; N–H)
Set (7)	(lactone with C(=O)–H)	(lactone with C(=O)–H)
Set (8)	CHO (decalin)	CHO, Cl (decalin)
Set (9)	$C_6H_5-\overset{O}{\overset{\|\|}{C}}-CH_3$	$C_6H_5-\overset{O}{\overset{\|\|}{C}}-C_6H_5$
Set (10)	$CH_3-\overset{O}{\overset{\|\|}{C}}-CH_2-CH_3$	$C_6H_5-\overset{O}{\overset{\|\|}{C}}-H$

8. Match the Column (I) and Column (II). (Matrix)

	Column (I)		Column (II)
(A)	Cyclobutanone $\xrightarrow[\text{traces of KOH}]{HCN} (A) \xrightarrow{LiAlH_4} (B) \xrightarrow[HCl]{NaNO_2} (C)$	(p)	Formation of six member ring takes place
(B)	Cyclopentanone $\xrightarrow{NH_2OH} (A) \xrightarrow{H^+} (B) \xrightarrow{LAH} (C)$	(q)	Final product is Ketone

(C)	$CH_3-\overset{O}{\overset{\parallel}{C}}-CH_2-CH_2-CH_2-\overset{O}{\overset{\parallel}{C}}-H \xrightarrow[\Delta]{HO^-} (A)$	**(r)**	Final product formed will give positive Tollens test
(D)	(cyclopentyl ring bearing OH)–C(OH)(Ph)(CH_3) $\xrightarrow[\Delta]{H^{\oplus}} (A)$	**(s)**	Final product formed will react with 2,4-DNP. (2,4-di-nitrophenyl hydrazine)

9. Consider reactions A through F. Those carbon atoms undergoing change, as part of a functional group, are marked as C^{12}, C^{14} or starred. In the cases shown, each carbon atom has either been reduced or oxidized. Your job is to identify the change in oxidation state that has occurred for each of the marked carbon.

	Reaction		C^{12}		C^{14}
A.	$CH_3\underset{12}{C}H=\underset{14}{C}H_2 \xrightarrow{Br_2} CH_3CHBrCH_2Br$		Reduced		Reduced
			Oxidized		Oxidized
B.	$CH_3\underset{12}{C}H=\underset{14}{C}H_2 \xrightarrow[(ii)\,H_2O_2,NaOH]{(i)\,B_2H_6} CH_3CH_2CH_2OH$		Reduced		Reduced
			Oxidized		Oxidized
C.	$CH_3CH_2\overset{*}{C}H=O \xrightarrow{NaBH_4} CH_3CH_2CH_2OH$		Reduced		
			Oxidized		
D.	$CH_3CH_2\overset{*}{C}H=O \xrightarrow[H_2O,\,pH>8]{Ag^{(+)}} CH_3CH_2CO_2H$		Reduced		
			Oxidized		
E.	$CH_3CO\underset{12}{C}H_2\underset{14}{C}O_2H \xrightarrow{Heat} CH_3COCH_3 + O=C=O$		Reduced		Reduced
			Oxidized		Oxidized
F.	$H_2\underset{12}{C}=\underset{14}{C}(OH)C_2H_5 \xrightarrow{tautomerization} H_3CCOC_2H_5$		Reduced		Reduced
			Oxidized		Oxidized

10. Consider the possible formation of an aldehyde or ketone product when each of the ten compounds in the column on the left is treated with each of the reagents shown in the top row. Check the designated answer box if you believe an aldehyde or ketone will be formed.

Assume that the reagents may be present in excess. For each checked reaction, try to draw the structure of the major product (s).

Starting	PCC $C_5H_5NHCrO_3Cl$	Jone's Reagent CrO_3 in aq. acid	$Pb(OAc)_4$ [or HIO_4]	(i) O_3, (ii) Zn dust	$H_3O^{\oplus}$	(i) BH_3 in THF (ii) H_2O_2 + NaOH
$C_6H_{11}-OH$ (cyclohexanol)						
$(CH_3)_2CH-C\equiv C-CH(CH_3)_2$						
$C_6H_5-CH_2-OH$						
C_6H_6						
$(CH_3)_2C=CH-CH_2-CH(OH)-CH_3$						
$CH_3-C(CH_3)_2-OH$						
$(H_3C)_2C=C(CH_3)_2$						
1-methylcyclopentene ($C_5H_7-CH_3$)						
$HO-CH_2-CH_2-CH_2-OH$						
$CH_3-C(OH)(CH_3)-CH(OH)-C_2H_5$						

11. Comprehension

Wittig reaction :

The reaction of a phosphorus ylide with an aldehyde (or) ketnoe introduces a carbon-carbon double bond is place of the carbonyl bond.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R + Ph_3P=CH_2 \longrightarrow R-\overset{\overset{\displaystyle CH_2}{\|}}{C}-R + Ph_3P=O$$

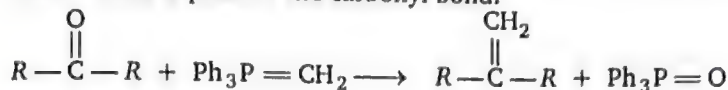
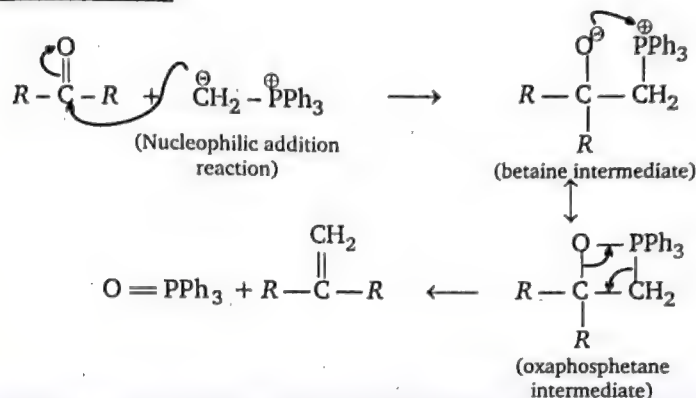
Mechanism :

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R + \overset{\ominus}{C}H_2-\overset{\oplus}{P}Ph_3 \longrightarrow R-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle O^{\ominus}}{|}}{C}}-CH_2-\overset{\oplus}{P}Ph_3$$

(Nucleophilic addition reaction)

(betaine intermediate)

$$O=PPh_3 + R-\overset{\overset{\displaystyle CH_2}{\|}}{C}-R \longleftarrow R-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle O-PPh_3}{|\quad\;\;|}}{C}}-CH_2$$

(oxaphosphetane intermediate)

Driving force of the reaction is high bond energy of $(P=O)$. $(\Delta H = -ve)$

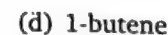
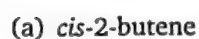
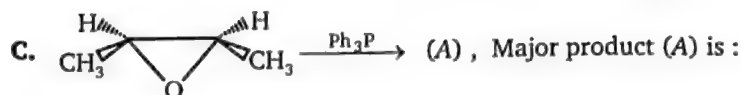
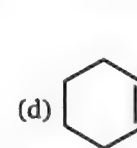
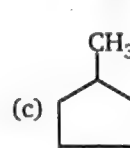
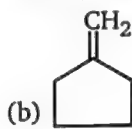
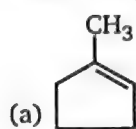
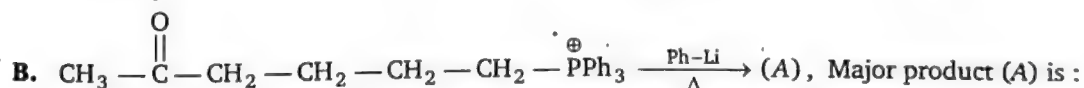
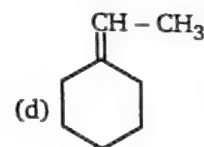
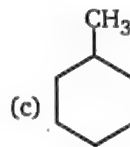
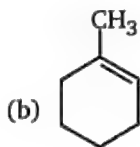
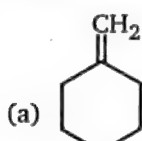
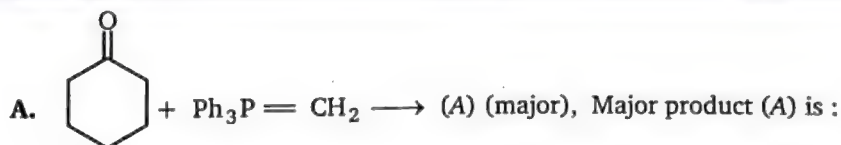
A. $+ Ph_3P=CH_2 \longrightarrow (A)$ (major), Major product (A) is :

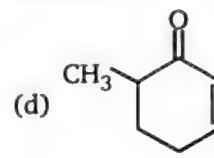
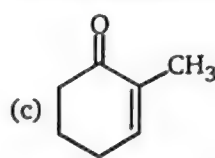
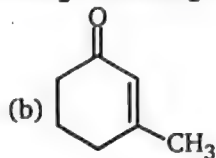
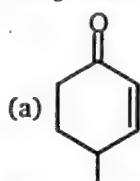
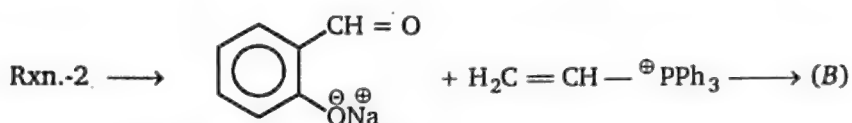
(a)
(b)
(c)
(d) [1-ethylidenecyclohexane: $=CH-CH_3$ on cyclohexane]

B. $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-CH_2-CH_2-\overset{\oplus}{P}Ph_3 \xrightarrow[\Delta]{Ph-Li} (A)$, Major product (A) is :

(a)
(b)
(c)
(d)

C. (2,3-dimethyloxirane with H, CH_3 substituents) $\xrightarrow{Ph_3P} (A)$, Major product (A) is :

(a) *cis*-2-butene (b) *trans*-2-butene (c) iso-butene (d) 1-butene

D. $CH_3-\overset{O}{\overset{\|}{C}}-(CH_2)_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{P}}(OEt)_2 \xrightarrow{NaH} (A)$ (cyclic). Product (*A*) is :

(a) (b) CH_3 (c) CH_3 (d) CH_3

E. Identify major product in given intramolecular Wittig reaction :

Rxn.-1 ⟶ $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH(CO_2Et)_2 + H_2C=CH-{}^{\oplus}PPh_3 \xrightarrow{NaH} (A)$

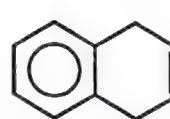
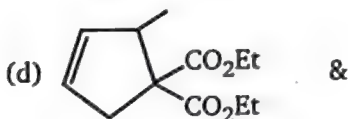
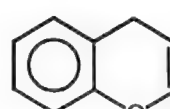
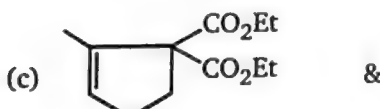
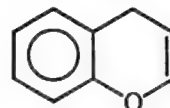
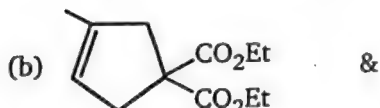
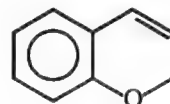
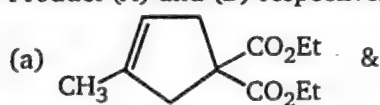
Rxn.-2 ⟶ $CH=O$, $\overset{\ominus}{O}\overset{\oplus}{Na}$ $+ H_2C=CH-{}^{\oplus}PPh_3 \longrightarrow (B)$

Product (*A*) and (*B*) respectively are :

(a) CH_3, CO_2Et, CO_2Et &

(b) CO_2Et, CO_2Et &

(c) CO_2Et, CO_2Et &

(d) CO_2Et, CO_2Et &

F. CH_2-Br, CH_2-Br $\xrightarrow[\text{(2) 2Ph-Li; (3) CHO-CHO}]{\text{(1) Ph}_3\text{P(2 mole)}}$ (*A*) ; product (*A*) is :

12. Match the column :

	Column (I) Conversion		Column (II) Reagent
(a)	$Me_3\overset{\oplus}{N}$ … CH_3 ⟶ $Me_3\overset{\oplus}{N}$ …	(p)	$NH_2/NH_2/HO^{\ominus}$, Δ (Wolff-Kishner reduction)
(b)	O … ⟶ O …	(q)	Zn(Hg), HCl (Clemmensen reduction)
(c)	O … ⟶ HO … OH	(r)	$LiAlH_4$
(d)	OH … O ⟶ OH …	(s)	None

13. Comprehension

$$(A) \xrightarrow[\text{dil. } H_2SO_4]{HgSO_4} (B) \xrightarrow[(2)\ H^{\oplus}/\Delta]{(1)\ NaBH_4} CH_3—\underset{\underset{CH—CH_3}{||}}{C}—CH_2—CH_3$$

A. Reactant (A) is :

(a) $CH_3—C \equiv C—\underset{\underset{CH_3}{|}}{CH}—CH_3$

(b) $HC \equiv C—C—\underset{\underset{C—C}{|}}{C}—C$

(c) $CH_3—\underset{\underset{CH_2—CH_3}{|}}{CH}—C \equiv CH$

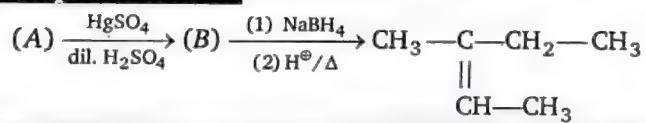
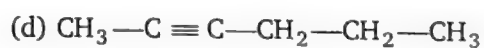
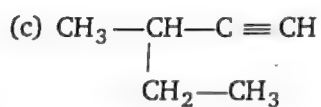
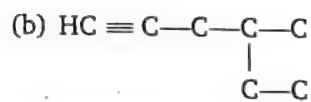
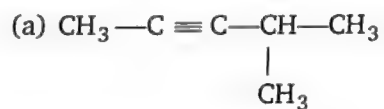
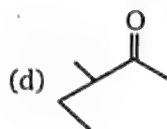
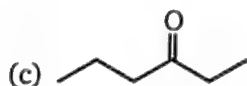
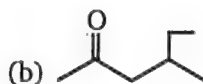
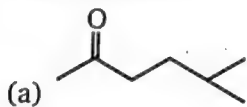
(d) $CH_3—C \equiv C—CH_2—CH_2—CH_3$

B. Product (B) is :

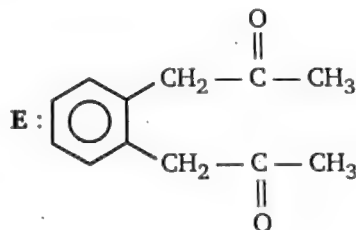
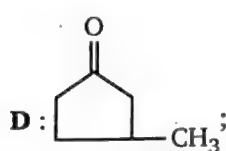
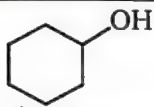
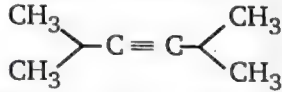
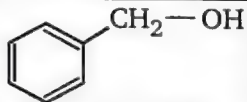
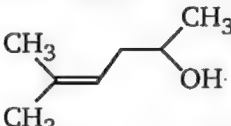
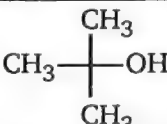
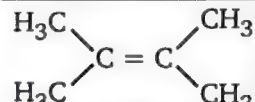
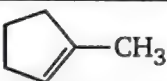
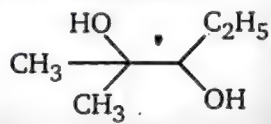
(a) O

(b) O

(c) O

(d) O

ANSWERS — LEVEL 2

1. A – l; B – g; C – n; D – k; E – h; F – c; G – j; H – f; I – m; J – d; K – e; L – b
2. i – A, B, C, E, F; ii – D, G, H; iii – B, E, F
3. a - p,r; b - r; c - s; d - p, r
4. **A** : $Ph-CH(OH)-CH_3$; **B** : $Ph-CH_2-COOH$; **C** : $Ph-CH=C(CH_3)_2$;

   D : 3-methylcyclopentanone (cyclopentanone with C=O and CH_3 on ring); **E** : benzene ring with two ortho substituents $CH_2-CO-CH_3$ and $CH_2-CO-CH_3$

5. A – b; B – b
6. $A+B+C=17$
7. set 1 – A; set 2 – A; set 3 – B; set 4 – B; set 5 – A; set 6 – B; set 7 – B; set 8 – B; set 9 – A; set 10 – B
8. A – p, q, s; B – p; C – p, q, s; D – p, q, s
9. A : both are oxidized; B : C^{12} is reduced, C^{14} is oxidized; C : reduced; D : oxidized E : C^{12} is reduced, C^{14} is oxidized; F : C^{12} is reduced, C^{14} is oxidized

10.

Compound	PCC $C_5H_5NHCrO_3Cl$	Jone's Reagent CrO_3 in aq. acid	$Pb(OAc)_4$ [or HIO_4]	(i) O_3, (ii) Zn dust	H_3O^+	(i) BH_3 in THF (ii) H_2O_2 + NaOH
Cyclohexanol ($C_6H_{11}OH$)	✓	✓	✗	✗	✗	✗
$(CH_3)_2CH{-}C{\equiv}C{-}CH(CH_3)_2$	✗	✗	✗	✓	✓	✓
$C_6H_5CH_2{-}OH$	✓	✓	✗	✓	✗	✗
Benzene	✗	✗	✗	✓	✗	✗
$(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}CH(OH)CH_3$	✓	✓	✗	✓	✓	✓
$(CH_3)_3C{-}OH$	✗	✗	✗	✗	✗	✗
$(H_3C)_2C{=}C(CH_3)_2$	✗	✗	✗	✓	✓	✓
1-Methylcyclopentene ($C_5H_7{-}CH_3$)	✗	✗	✗	✓	✓	✓
$HO{-}CH_2CH_2CH_2CH_2{-}OH$	✓	✓	✗	✗	✗	✗
$CH_3{-}C(OH)(CH_3){-}CH(OH){-}C_2H_5$	✓	✓	✓	✗	✗	✗

11. A – a; B – a; C – b; D – b; E – a; F – b

12. a – q; b – s; c – r; d – p

13. **A.** (c) **B.** (d)

8 ALDOL AND CANNIZARO REACTION

LEVEL-1

1. Compound *A* and *B*, both were treated with NaOH, producing a single compound *C*.

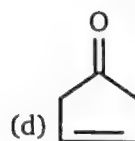
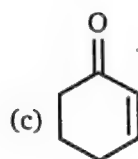
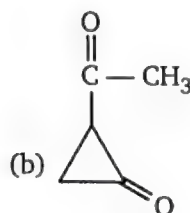
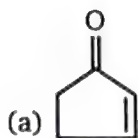
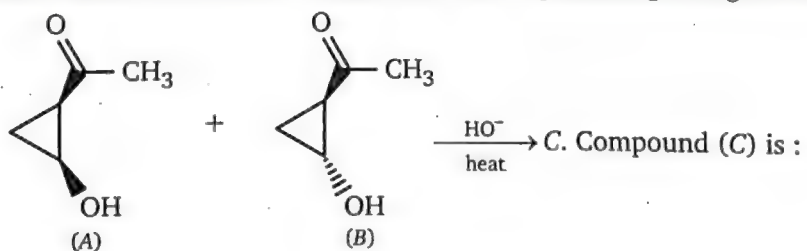
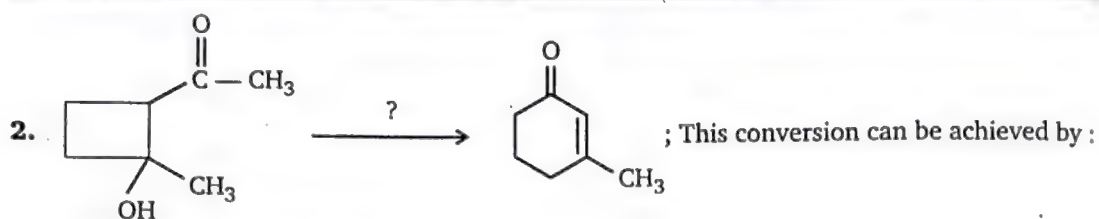
O, CH_3, OH (*A*) + O, CH_3, OH (*B*) $\xrightarrow[\text{heat}]{HO^-}$ *C*. Compound (*C*) is :

(a) O

(b) O, C — CH_3, O

(c) O

(d) O

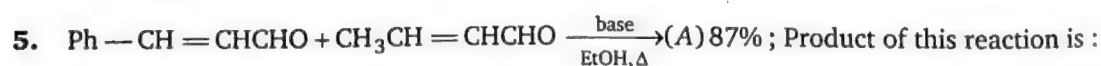
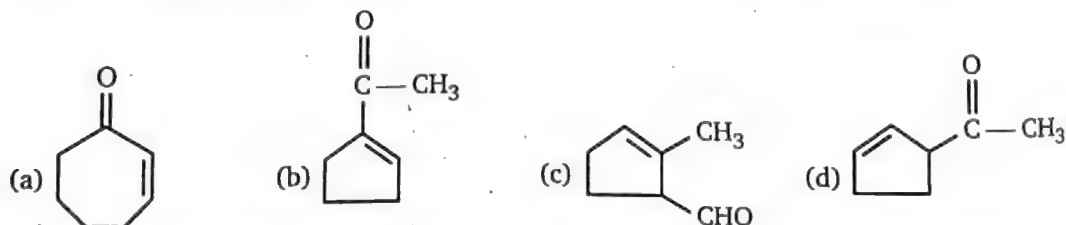
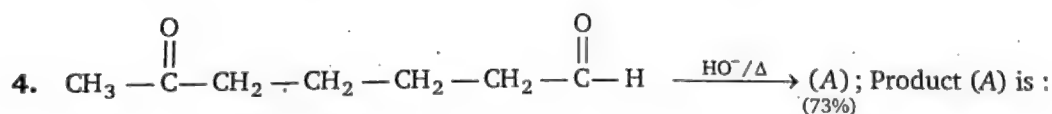
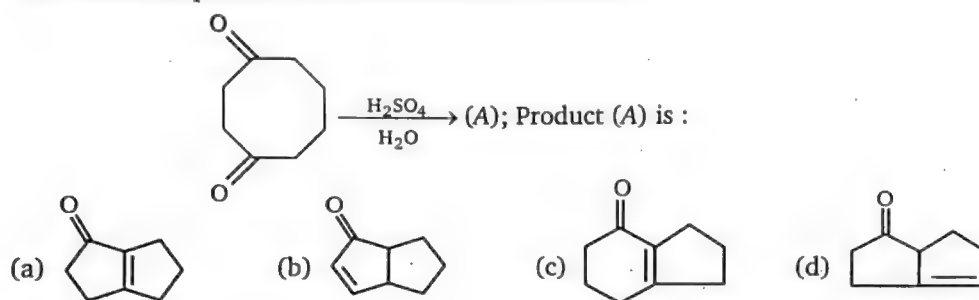
2. $\xrightarrow{?}$; This conversion can be achieved by :

(a) Dehydration, Hydrolysis
(b) Retro aldol and further condensation
(c) Perkin condensation & Clemmensen reduction
(d) Clemmensen and Perkin condensation

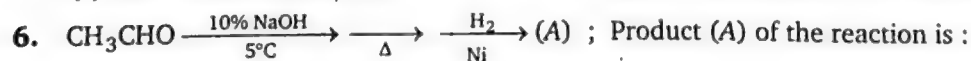
3. This is an example of an intramolecular aldol reaction :

$\xrightarrow[H_2O]{H_2SO_4}$ (*A*); Product (*A*) is :

(a) (b) (c) (d)

4. $CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{||}{C}}-H \xrightarrow[(73\%)]{HO^-/\Delta}$ (*A*); Product (*A*) is :

5. $Ph-CH=CHCHO + CH_3CH=CHCHO \xrightarrow[EtOH, \Delta]{base} (A)$ 87% ; Product of this reaction is :

(a) $Ph-(CH=CH)_2-CHO$
(b) $Ph-(CH=CH)_3CHO$
(c) $Ph-(CH=CH)_4CHO$
(d) $Ph-CH=CH-CH=CH-CH_3$

6. $CH_3CHO \xrightarrow[5°C]{10\% \ NaOH} \xrightarrow{\Delta} \xrightarrow[Ni]{H_2} (A)$; Product (*A*) of the reaction is :

(a) propanol (b) ethanol (c) butanol (d) pentanol

7. $(A) \xrightarrow[\Delta]{NaOH}$ [1-acetylcyclopentene: cyclopentene ring bearing $-\overset{O}{\overset{\|}{C}}-CH_3$]. Reactant (A) is :

(a) $CH_3-\overset{O}{\overset{\|}{C}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}-CH_3$

(b) $CH_3-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-H$

(c) $H-\overset{O}{\overset{\|}{C}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}-H$

(d) $CH_3-\overset{O}{\overset{\|}{C}}-(CH_2)_4-CH_2-OH$

8. $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-CHO \xrightarrow{KOH,\ H_2O} (A)$; Product A is:

(a) (b) (c) (d)

9. [2-methylcyclohexanone] $\xrightarrow[CH_3-CH_2-I]{LDA} (A)$ (major) ; Product A is:

(a) (b) (c) (d)

10. The reaction ,

[benzene-1,2-dicarbaldehyde: benzene ring with CHO, CHO] + conc. NaOH $\xrightarrow{heat}$, products Identify the product.

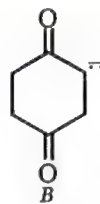
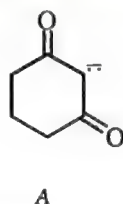
(a) [benzene ring with $CH(OH)_2$, $CH(OH)_2$]

(b) [benzene ring fused to five-membered ring containing O]

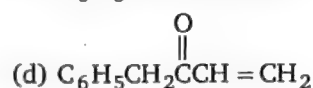
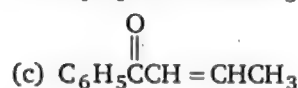
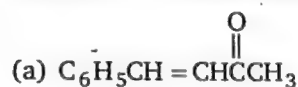
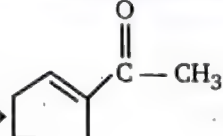
(c) [benzene ring with CH_2OH, COO^-]

(d) [benzene ring with COO^-, COO^-]

11. Compare enolate *A* with enolate *B*.

A B

Which of the following statements is true ?

(a) *A* is more stable than *B*
(b) *A* and *B* have the same stability
(c) *B* is more stable than *A*
(d) No comparison of stability can be made

12. Benzalacetone is the product of mixed aldol condensation between benzaldehyde ($C_6H_5CH=O$) and acetone [$(CH_3)_2C=O$]. What is its structure ?

(a) $C_6H_5CH=CH\overset{O}{\overset{\|}{C}}CH_3$
(b) $C_6H_5CH=C(CH_3)_2$
(c) $C_6H_5\overset{O}{\overset{\|}{C}}CH=CHCH_3$
(d) $C_6H_5CH_2\overset{O}{\overset{\|}{C}}CH=CH_2$

13. Identify the major product *P* in the following reaction:

$$+ \quad Cl\text{—}CH_2CHO \xrightarrow{\text{aq. NaOH}} P$$

(a) (b) (c) (d)

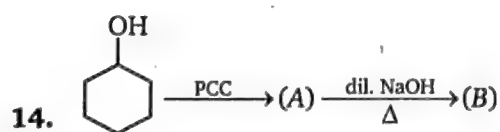
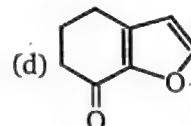
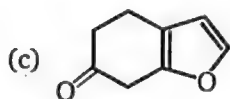
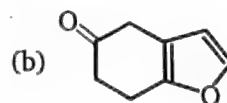
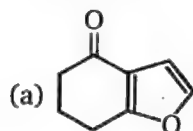
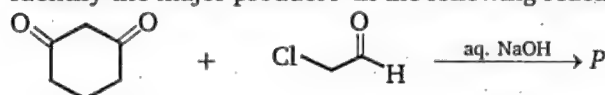
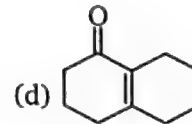
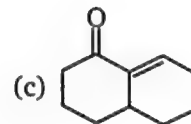
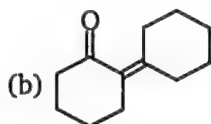
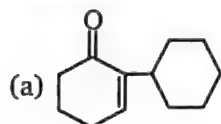
14. $\xrightarrow{\text{PCC}} (A) \xrightarrow[\Delta]{\text{dil. NaOH}} (B)$

OH

Product (*B*) is:

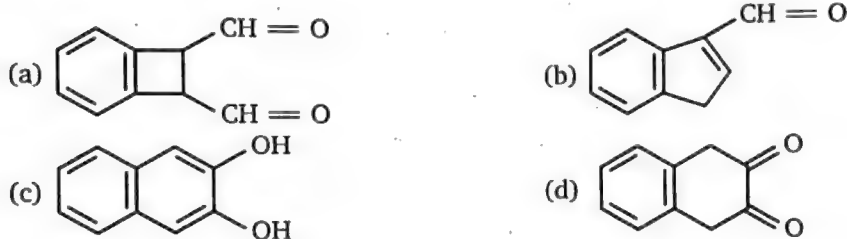
(a) (b) (c) (d)

15. $(A) \xrightarrow[\text{(ii) Zn, } H_2O]{\text{(i) } O_3} (B) \xrightarrow[\Delta]{\text{NaOH}}$ [cyclopentene bearing $\overset{O}{\overset{\|}{C}}-CH_3$] the reactant (A) will be :

(a) [1-methylcyclohexene] (b) [methylcyclohexene] (c) [methylcyclohexene] (d) [methylenecyclohexene, CH_2]

16. Identify the principal product of the following reaction?

[benzene with two $CH_2CH=O$ groups] $\xrightarrow[\text{ethanol, water, heat}]{\text{NaOH}} H_2O + ?$

(a) [benzocyclobutene with two $CH=O$ groups] (b) [indene with $CH=O$]

(c) [naphthalene with two OH groups] (d) [tetralin-2,3-dione]

17. Which one of the following compounds is the best choice for being prepared by an efficient mixed aldol addition reaction?

(a) $C_6H_5-\overset{OH}{\underset{CH_3}{C}}H_2\overset{O}{\overset{\|}{C}}H$, i.e. $C_6H_5-C(OH)(CH_3)CH_2CHO$

(b) $C_6H_5-\overset{O}{\overset{\|}{C}}CHCH_3$ with CH_2OH on CH

(c) $C_6H_5-CH_2\overset{O}{\overset{\|}{C}}CHCH_3$ with $HO-C(CH_3)_2-$ on CH

(d) $C_6H_5-\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}H$

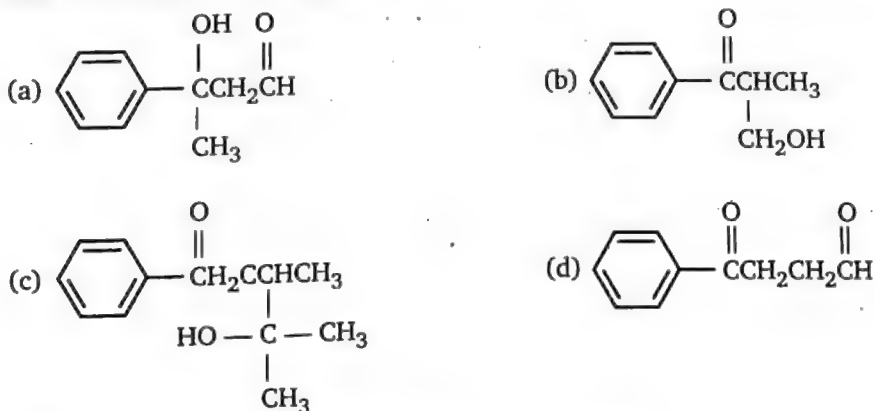
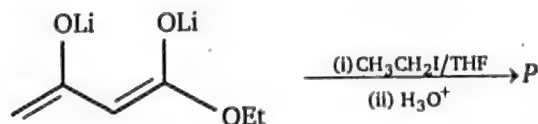
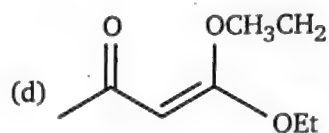
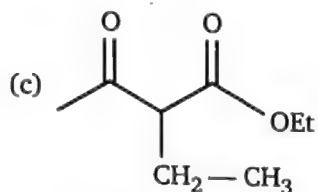
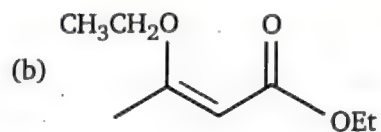
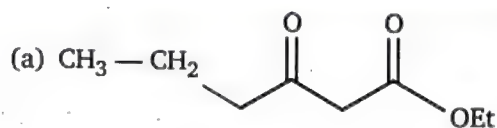
18. Identify the major product *P* in the following reaction:

[$CH_2=C(OLi)-CH=C(OLi)-OEt$] $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3CH_2I/THF} P$

(a) $CH_3-CH_2-CH_2-CO-CH_2-CO-OEt$

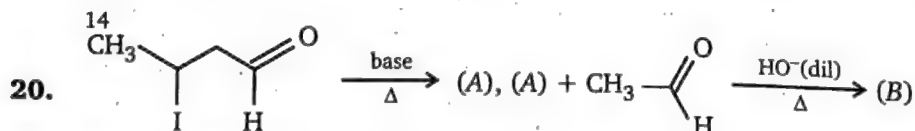
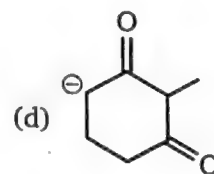
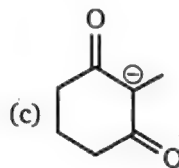
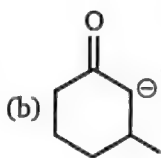
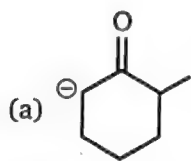
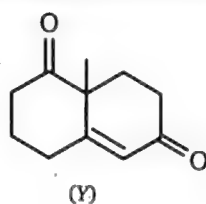
(b) $CH_3-C(OCH_2CH_3)=CH-CO-OEt$

(c) $CH_3-CO-CH(CH_2-CH_3)-CO-OEt$

(d) $CH_3-CO-CH=C(OCH_3CH_2)-OEt$

19. The enolate ion that reacts with 3-buten-2-one to form (*Y*) is :

(*Y*)

(a) (b) (c) (d)

20. $\overset{14}{C}H_3-CH(I)-CH_2-CHO \xrightarrow[\Delta]{\text{base}} (A), (A) + CH_3-CHO \xrightarrow[\Delta]{HO^-(\text{dil})} (B)$

Product (*B*) in the above reaction is :

(a) $CH_3-\overset{14}{C}H=CH-CH=CH-CHO$

(b) $\overset{14}{C}H_3-CH=CH-CH=CH-CHO$

(c) $\overset{14}{C}H_3-CH(Br)-C(CHO)=CH-CH_3$

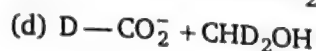
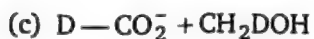
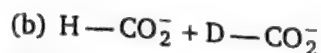
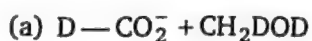
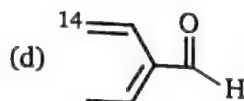
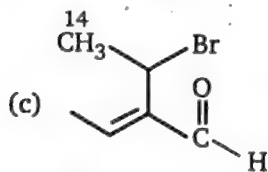
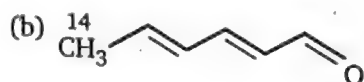
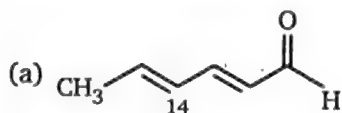
(d) $\overset{14}{C}H_2=CH-C(CHO)=CH-CH_3$

21. $H-\overset{O}{\overset{||}{C}}-D \xrightarrow[(50\%)]{HO^-}$; Product of this Cannizaro reaction is :

(a) $D-CO_2^- + CH_2DOD$

(b) $H-CO_2^- + D-CO_2^-$

(c) $D-CO_2^- + CH_2DOH$

(d) $D-CO_2^- + CHD_2OH$

22. An organic compound with the molecular formula $C_9H_{10}O$ forms a 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizaro reaction, on vigorous oxidation it gives 1,2-benzenedicarboxylic acid. Structure of organic compound is:

(a) (4-ethylbenzene ring) CHO

(b) (2-ethylbenzene ring) CHO

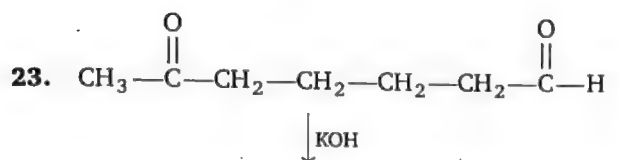
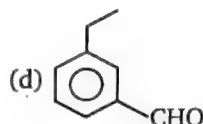
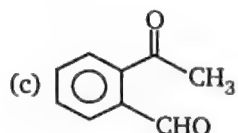
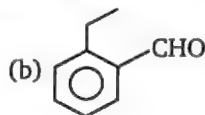
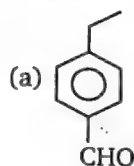
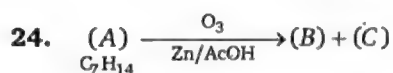
(c) (benzene ring) $\overset{O}{\overset{\|}{C}}$ CH_3, CHO

(d) (3-ethylbenzene ring) CHO

23. $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{KOH}$

Number of intramolecular aldol condensation product is :

(a) 1 (b) 2 (c) 3 (d) 4

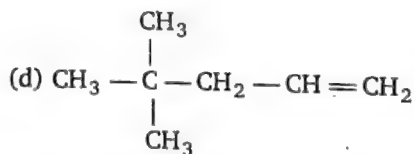
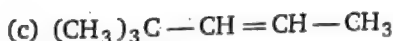
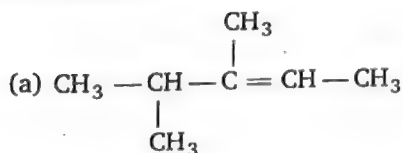
24. $\underset{C_7H_{14}}{(A)} \xrightarrow[Zn/AcOH]{O_3} (B) + (C)$

Compound (A) exist in geometrical isomers and (B) gives Cannizaro reaction.

(A) will be :

(a) $CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{C}}=CH-CH_3$

(b) $(CH_3)_3CCH_2-CH=CH_2$

(c) $(CH_3)_3C-CH=CH-CH_3$

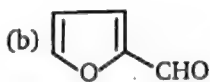
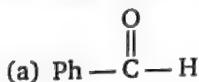
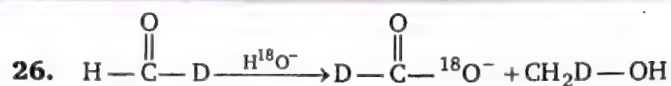
(d) $CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-CH=CH_2$

25. Which of the following compounds will not undergo Cannizaro reaction, when treated with 50% aqueous alkali?

(a) $Ph-\overset{O}{\overset{\|}{C}}-H$

(b)

(c) Me_2CHCHO

(d) $Ph-CH_2-CHO$

26. $H-\overset{O}{\overset{\|}{C}}-D \xrightarrow{H^{18}O^-} D-\overset{O}{\overset{\|}{C}}-{}^{18}O^- + CH_2D-OH$

Above reaction is known as :

(a) Cannizaro reaction, Disproportionation reaction
(b) Tischenko reaction, Disproportionation reaction
(c) Cross Cannizaro reaction, Redox reaction
(d) Tischenko reaction, Redox reaction

27. 2-Methylcyclohexanone + $CH_2=CH-C(=O)-CH_3$ $\xrightarrow[\text{(Conjugate–addition)}]{HO^-}$ (A) ; Product (A) is :

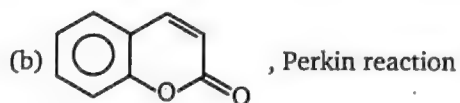
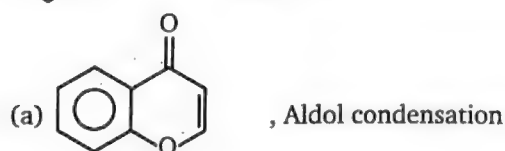
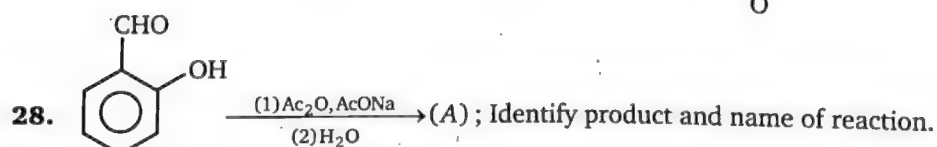
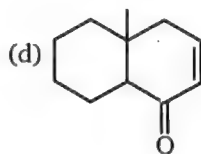
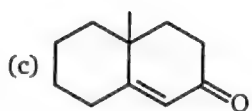
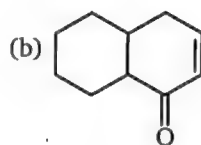
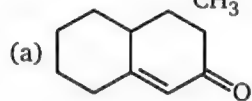
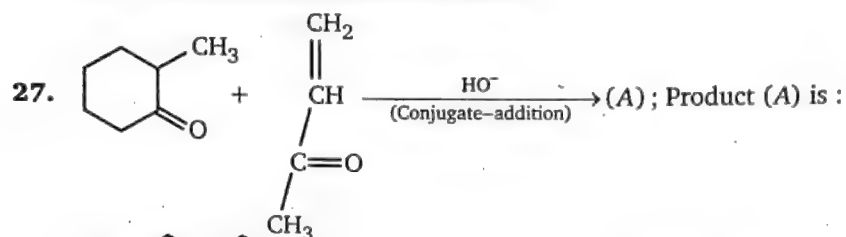
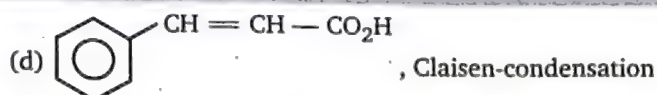
(a) (b) (c) (d)

28. Salicylaldehyde (CHO, OH) $\xrightarrow[(2)H_2O]{(1)Ac_2O, AcONa}$ (A) ; Identify product and name of reaction.

(a) , Aldol condensation

(b) , Perkin reaction

(c) , Cannizaro reaction

(d) $C_6H_5-CH=CH-CO_2H$, Claisen-condensation

29. Choose the most reasonable reaction intermediate for the following reaction.

(3-ethylcyclopent-2-en-1-one) $\underset{\text{(cat.)}}{\overset{HO^-}{\rightleftharpoons}}$ (2,3-dimethylcyclopent-2-en-1-one)

(a) $CH_3COCH=CHCH_2CH_3$
(b) $CH_3CH_2COCH=CHCH_3$
(c) $CH_3COCH_2CH_2COCH_2CH_3$
(d) None of these

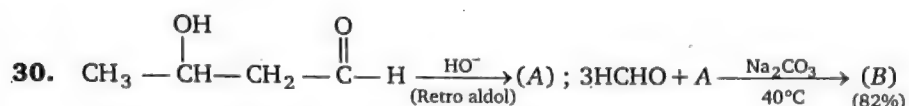
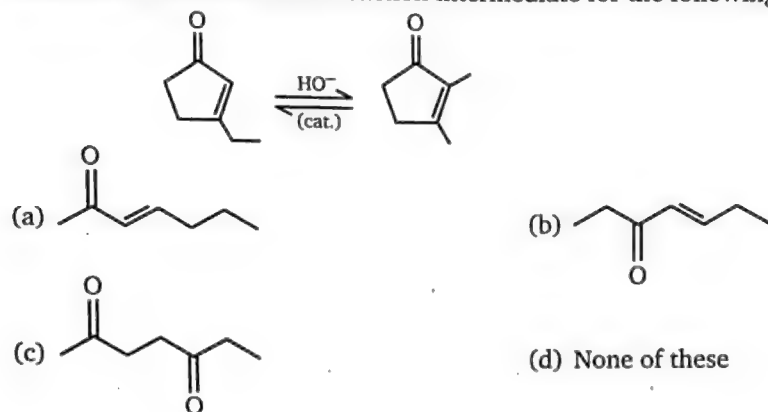
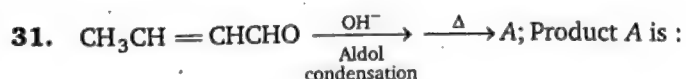
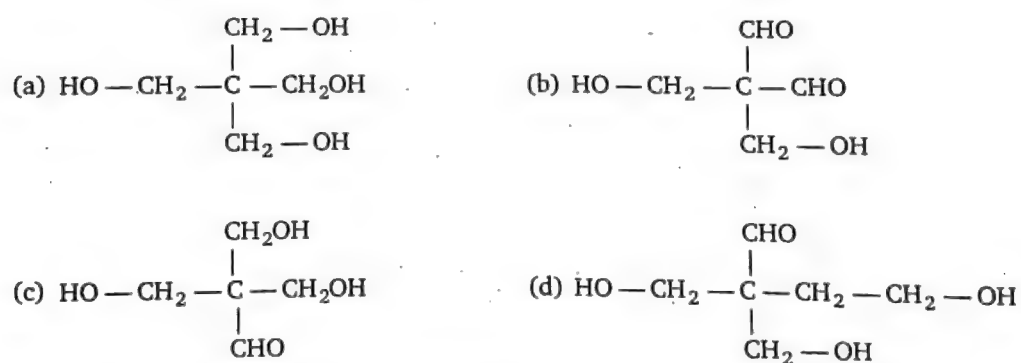
30. $CH_3-\underset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\text{(Retro aldol)}]{HO^-} (A)$; $3HCHO + A \xrightarrow[40°C]{Na_2CO_3} (B)$ (82%)

Product (*B*) of the above reaction is :

(a) $HO-CH_2-C(CH_2-OH)(CH_2-OH)-CH_2OH$

(b) $HO-CH_2-C(CHO)(CH_2-OH)-CHO$

(c) $HO-CH_2-C(CH_2OH)(CHO)-CH_2OH$

(d) $HO-CH_2-C(CHO)(CH_2-OH)-CH_2-CH_2-OH$

31. $CH_3CH=CHCHO \xrightarrow[\text{Aldol condensation}]{OH^-} \xrightarrow{\Delta} A$; Product *A* is :

(a) $CH_3(CH=CH)_3CHO$
(b) $CH_3CH_2CH_2(CH=CH)_2CHO$
(c) $CH_3(CH_2CH_2)_3CH=CH-CHO$
(d) none is correct

32. (A) $\xrightleftharpoons[H_2O]{HO^{\ominus}}$ B. (A) and (B) are isomer : Identify (B).

(a) (b)

(c) (d)

33. OH $\xrightarrow[\Delta]{H^+}$ (A) $\xrightarrow[Zn]{O_3}$ (B) $\xrightarrow[\Delta]{HO^-}$ (C) (72%) ; Product (C) is :

(a) (b)

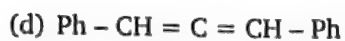
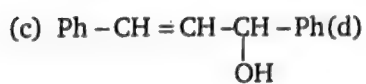
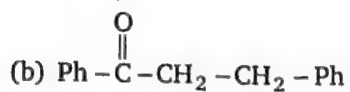
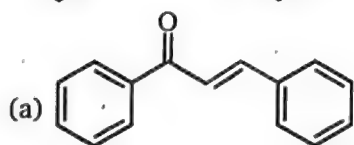
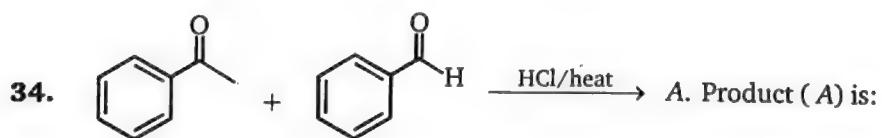
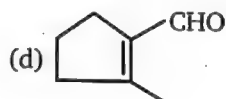
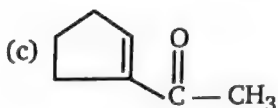
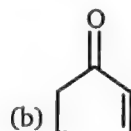
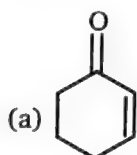
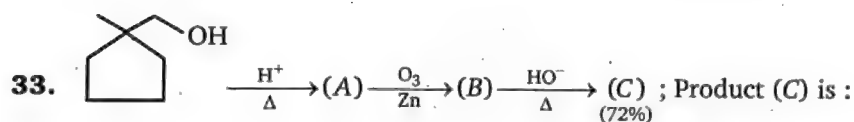
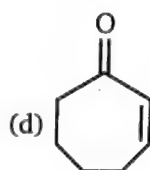
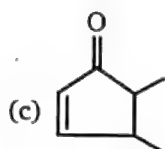
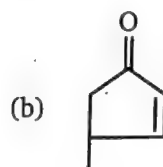
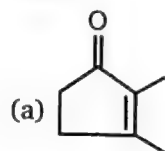
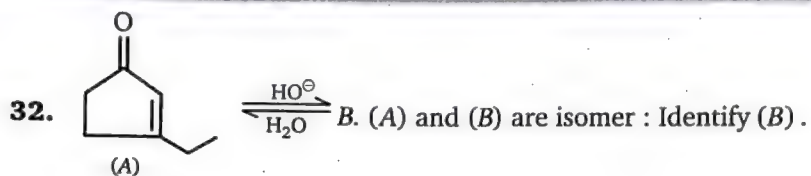
(c) $\overset{O}{\overset{\|}{C}}-CH_3$ (d) CHO

34. + H $\xrightarrow{HCl/heat}$ A. Product (A) is:

(a)

(b) $Ph-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-Ph$

(c) $Ph-CH=CH-\underset{OH}{\underset{|}{CH}}-Ph$(d)

(d) $Ph-CH=C=CH-Ph$

35. Which of the following reactant on reaction with conc. NaOH followed by acidification gives the following lactone as the product ?

(a) $C_6H_4(COOCH_3)(CO_2H)$ (b) $C_6H_4(CO_2H)(CHO)$

(c) $C_6H_4(CHO)(CHO)$ (d) $C_6H_4(CO_2H)(CO_2H)$

36. $\xrightarrow{NaOH}$ Product; Product is:

(a) (b)

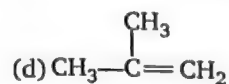
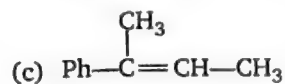
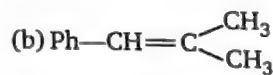
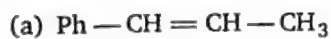
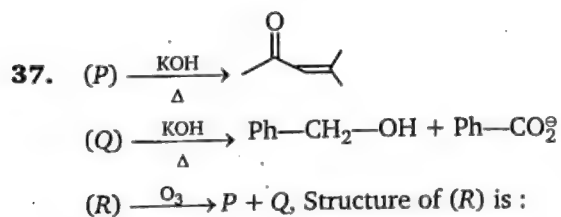
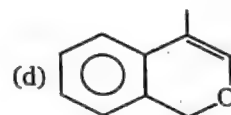
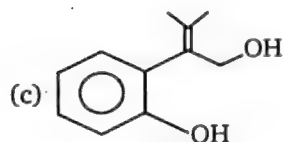
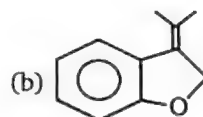
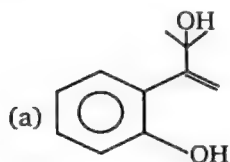
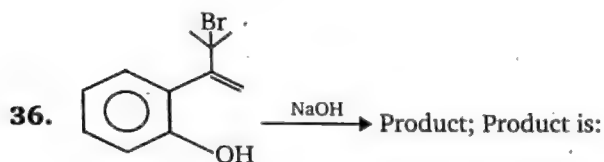
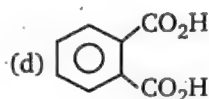
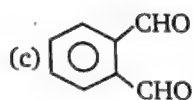
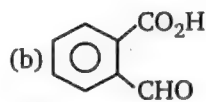
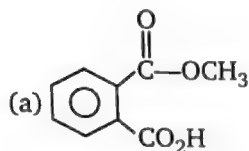
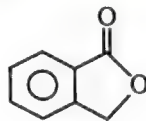
(c) (d)

37. (*P*) $\xrightarrow[\Delta]{KOH}$

(*Q*) $\xrightarrow[\Delta]{KOH}$ Ph—CH_2—OH + Ph—$CO_2^{\ominus}$

(*R*) $\xrightarrow{O_3}$ *P* + *Q*, Structure of (*R*) is :

(a) Ph — CH = CH — CH_3 (b) Ph—CH=C(CH_3)CH_3

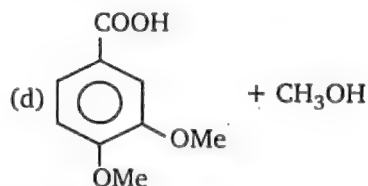
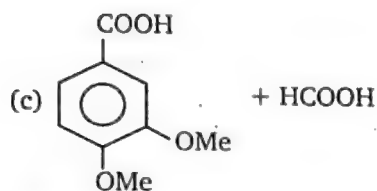
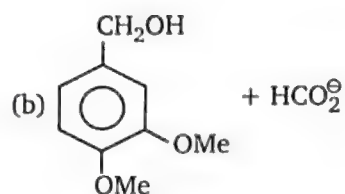
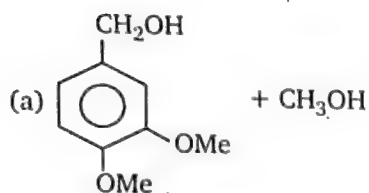
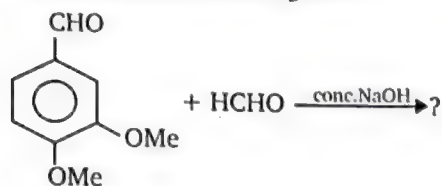
(c) Ph—C(CH_3)=CH—CH_3 (d) CH_3—C(CH_3)=CH_2

38. The following reaction gives:

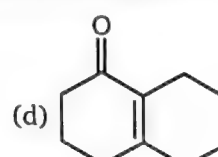
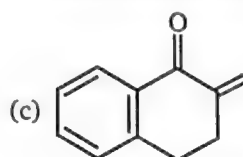
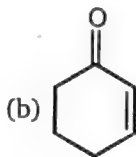
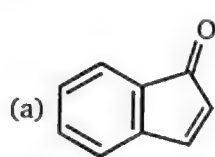
CHO, OMe, OMe (benzene ring) + HCHO $\xrightarrow{\text{conc.NaOH}}$?

(a) CH_2OH, OMe, OMe (benzene ring) + CH_3OH

(b) CH_2OH, OMe, OMe (benzene ring) + $HCO_2^{\ominus}$

(c) COOH, OMe, OMe (benzene ring) + HCOOH

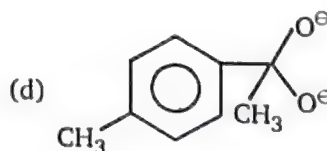
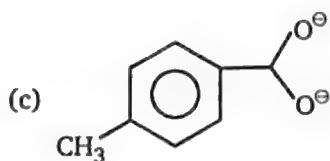
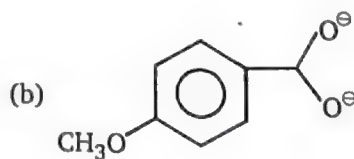
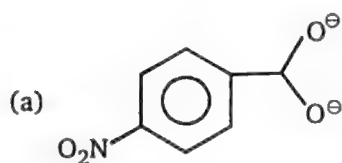
(d) COOH, OMe, OMe (benzene ring) + CH_3OH

39. Which of the following is not the product of an intramolecular aldol condensation ?

(a) O (b) O (c) O (d) O

40. x = no. of compound better hydride donor than $Ph-\underset{H}{\overset{O^{\ominus}}{C}}-O^{\ominus}$

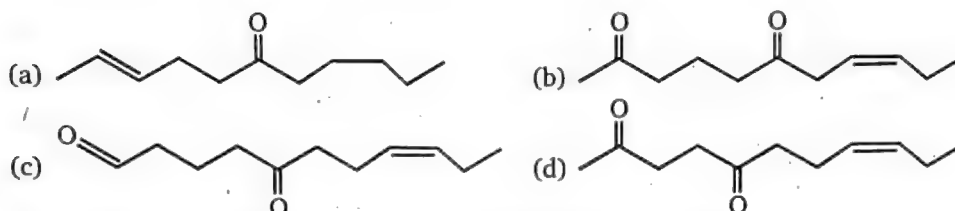
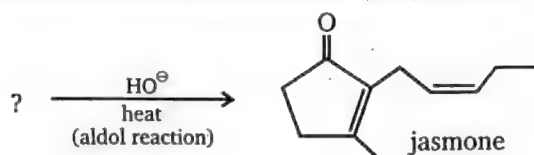
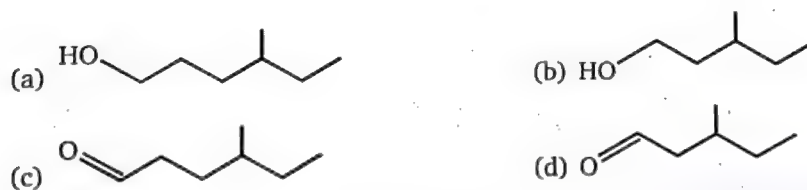
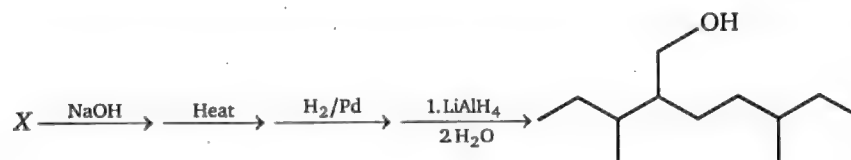
(a) O_2N, $O^{\ominus}$, $O^{\ominus}$

(b) CH_3O, $O^{\ominus}$, $O^{\ominus}$

(c) CH_3, $O^{\ominus}$, $O^{\ominus}$

(d) CH_3, $O^{\ominus}$, $O^{\ominus}$, CH_3

41. Choose the reactant whose aldol reaction would give jasmone.

? $\xrightarrow[\text{heat (aldol reaction)}]{HO^{\ominus}}$ jasmone

(a) (b) (c) (d)

42. Compound *X* undergoes the following reaction sequence. What is the structure of compound *X* ?

$X \xrightarrow{NaOH} \xrightarrow{Heat} \xrightarrow{H_2/Pd} \xrightarrow[2H_2O]{1. LiAlH_4}$ OH

(a) HO (b) HO

(c) O (d) O

43. Predict the major product of the following reaction sequence

CH_3 + NaOH $\xrightarrow{H_3C\text{-}C_6H_4\text{-}CHO}$ $\xrightarrow[Heat]{-H_2O}$ $\xrightarrow[2.\ H_2O]{1.\ \text{OLi}}$

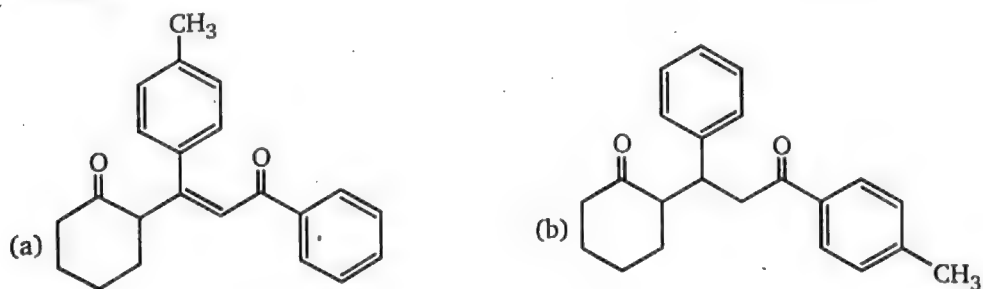
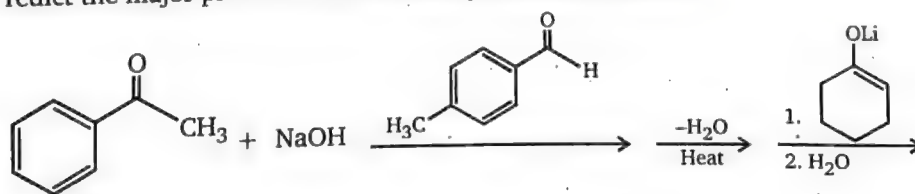
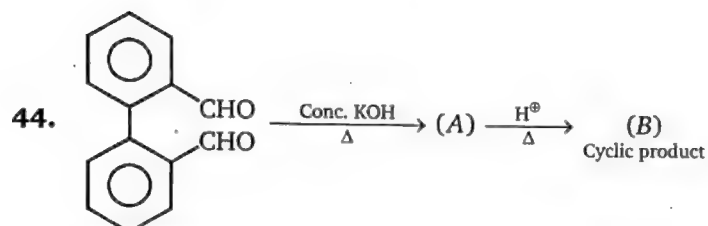
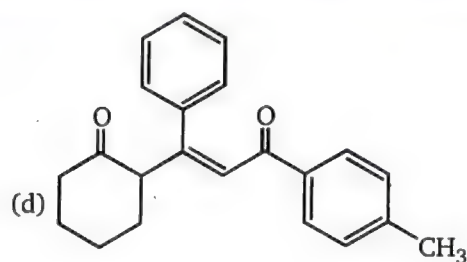
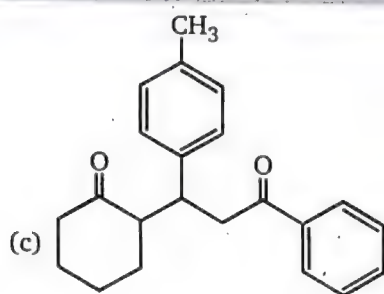
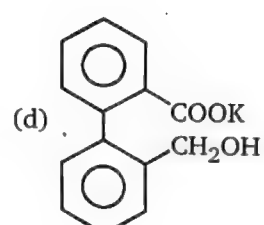
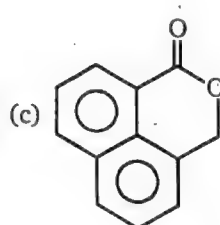
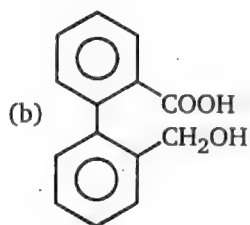
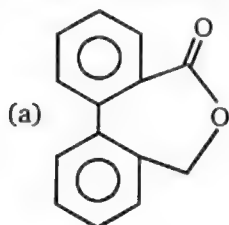
(a) CH_3 (b) CH_3

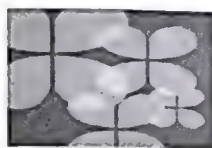
(c) [structure: 2-substituted cyclohexanone with $CH(C_6H_4CH_3\text{-}p)CH_2COC_6H_5$]

(d) [structure: 2-substituted cyclohexanone with $C(C_6H_5)=CHCOC_6H_4CH_3\text{-}p$]

44. [Biphenyl-2,2'-dicarbaldehyde: CHO, CHO] $\xrightarrow[\Delta]{\text{Conc. KOH}}$ (A) $\xrightarrow[\Delta]{H^{\oplus}}$ (B) Cyclic product

Structure of (B) is :

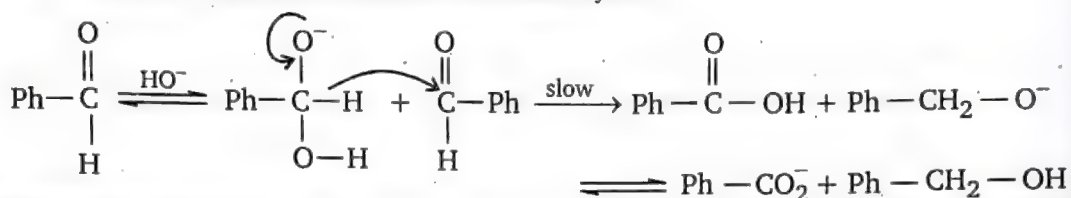
(a) [cyclic lactone: biphenyl bridged by C(=O)–O–CH$_2$] (b) [biphenyl with COOH, CH_2OH] (c) [naphthalene-fused lactone] (d) [biphenyl with COOK, CH_2OH]

ANSWERS — LEVEL 1

1.	(a)	**2.**	(b)	**3.**	(a)	**4.**	(b)	**5.**	(b)	**6.**	(c)	**7.**	(b)	**8.**	(b)
9.	(b)	**10.**	(c)	**11.**	(a)	**12.**	(a)	**13.**	(a)	**14.**	(b)	**15.**	(a)	**16.**	(b)
17.	(b)	**18.**	(a)	**19.**	(c)	**20.**	(a)	**21.**	(c)	**22.**	(b)	**23.**	(c)	**24.**	(c)
25.	(d)	**26.**	(a)	**27.**	(c)	**28.**	(b)	**29.**	(c)	**30.**	(c)	**31.**	(a)	**32.**	(a)
33.	(c)	**34.**	(a)	**35.**	(c)	**36.**	(b)	**37.**	(b)	**38.**	(b)	**39.**	(c)	**40.**	(b,c)
41.	(d)	**42.**	(d)	**43.**	(c)	**44.**	(a)								

LEVEL-2

1. Comprehension

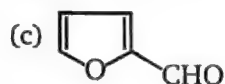
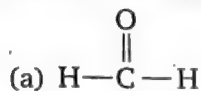
Mechanism of Cannizzaros reaction of benzaldehyde is

$$Ph-\overset{O}{\overset{||}{C}}-H \xrightleftharpoons{HO^-} Ph-\underset{O-H}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-H + \underset{H}{\underset{|}{\overset{O}{\overset{||}{C}}}}-Ph \xrightarrow{slow} Ph-\overset{O}{\overset{||}{C}}-OH + Ph-CH_2-O^-$$

$$\rightleftharpoons Ph-CO_2^- + Ph-CH_2-OH$$

A. Which of the following reactants can undergo Cannizaro's reaction.?

(a) $H-\overset{O}{\overset{||}{C}}-H$

(b) R_3CCHO

(c) CHO

(d) All of these

B. Order of the above reaction is:

(a) 1

(b) 2

(c) 3

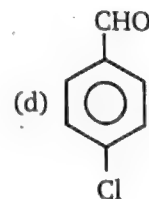
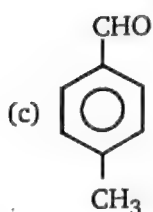
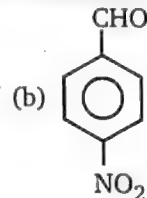
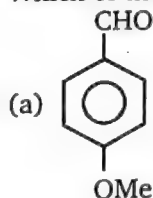
(d) 4

C. Which of the following is best hydride donor in Cannizaro's reaction?

(a) CHO / OMe

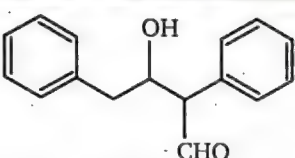
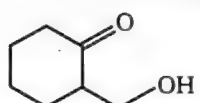
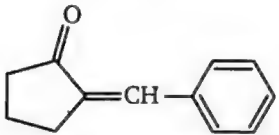
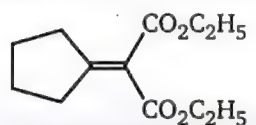
(b) CHO / NO_2

(c) CHO / CH_3

(d) CHO / Cl

D. Cannizaro's reaction is:

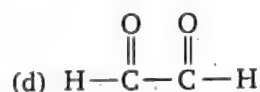
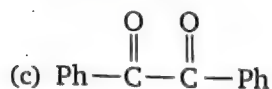
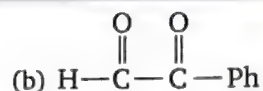
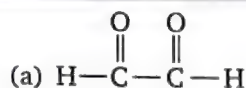
(a) Reduction

(b) Disproportionation reaction

(c) Oxidation

(d) Ion - exchange reaction

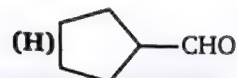
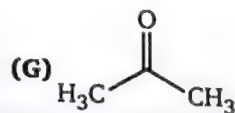
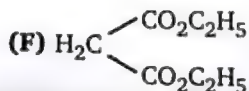
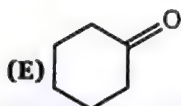
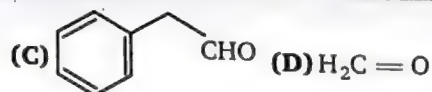
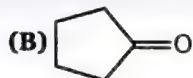
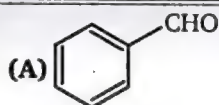
E. Which of the following cannot undergo intramolecular Cannizaro's reaction?

(a) $H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$ (b) $H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-Ph$

(c) $Ph-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-Ph$ (d) $H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$

2. Aldol condensation proceeds by carbon-carbon bond formation between an enolate donor and a carbonyl acceptor. For each of the following aldol products (a through e) select a donor and an acceptor compound from the list at the bottom of the page (compounds A through H). Write the letter corresponding to your selection in the appropriate answer box.

	Aldol Product	Donor	Acceptor
a.	$PhCH_2CH(OH)CH(CHO)Ph$ (OH, CHO)		
b.	2-(hydroxymethyl)cyclohexanone (O, OH)		
c.	2-benzylidenecyclopentanone (O, =CH–Ph)		
d.	$(CH_3)_2C(OH)CH_2COCH_3$		
e.	cyclopentylidene malonate ($CO_2C_2H_5$, $CO_2C_2H_5$)		

(A) C_6H_5CHO (benzaldehyde) (B) cyclopentanone (=O) (C) $C_6H_5CH_2CHO$ (D) $H_2C=O$

(E) cyclohexanone (F) $H_2C(CO_2C_2H_5)_2$ (G) $H_3C-\overset{O}{\overset{\|}{C}}-CH_3$ (H) cyclopentyl–CHO

3. Comprehension

During an experimental workup procedure, a chemist treated a starting material with NaOH in the solvent acetone [$(CH_3)_2C=O$]; however, the starting material was recovered unreacted. Instead, the chemist isolated a small amount of Product *A* (shown below).

Product A

The chemist determined that Product A resulted from the aldol self-condensation of acetone. Product A was identified based on the following observations.

Observations about Product A

1. Elemental analysis of Product A indicated that it consisted only of carbon, hydrogen, and oxygen.
2. product A had a molecular weight of 116 g/mol.
3. Product A was a methyl ketone because it gave a positive iodoform test.
4. When product A was treated with Br_2 in CCl_4, the red bromine colour persisted, because no carbon-carbon double bonds were present to react with the bromine.

The structure of Product A was further confirmed when treatment with hot sulfuric acid resulted in the corresponding dehydration product, Product B.

A. What is the molecular weight of a compound that undergoes an aldol self-condensation reaction to result in a β-hydroxy ketone with a molecular weight of 144 ?

(a) 70 g/mol (b) 72 g/mol
(c) 74 g/mol (d) 76 g/mol

B. The aldol self-condensation of acetone is an equilibrium that favours acetone over its condensation product. Which of the following experimental modifications is most likely to shift the position of equilibrium toward Product A ?

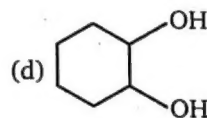
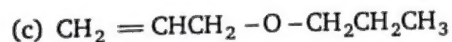
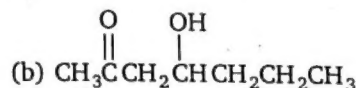
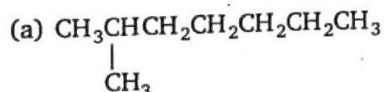
(a) Using only a catalytic amount of NaOH
(b) Using only a catalytic amount of acetone
(c) Removing Product A as it is formed
(d) Increasing the reaction temperature to the boiling point of acetone

C. Based only on observation 1 and 2, which of the following compounds could have been Product A ?

(a) $CH_3CH(CH_3)CH_2CH_2CH_2CH_2CH_3$

(b) $CH_3C(=O)CH_2CH(OH)CH_2CH_2CH_3$

(c) $CH_2=CHCH_2-O-CH_2CH_2CH_3$

(d) cyclohexane-1,2-diol (ring with two OH groups on adjacent carbons)

D. When a drop of Br_2 in CCl_4 is added to Product B, the resulting solution will be :

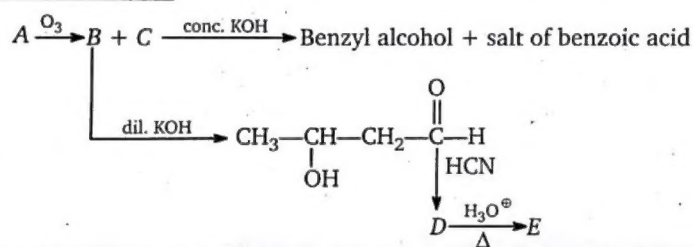
(a) colourless, because Product B does not contain a carbon-carbon double bond
(b) colourless, because Product B contains a carbon-carbon double bond
(c) red, because Product B does not contain a carbon-carbon double bond
(d) red, because Product B contains a carbon-carbon double bond

E. Which of the following compounds from the passage will give a positive iodoform test ?

(a) Product A only
(b) Product A and Product B
(c) Product A and acetone only
(d) Product A, Product B, and acetone

4. Comprehension

$$A \xrightarrow{O_3} B + C \xrightarrow{\text{conc. KOH}} \text{Benzyl alcohol + salt of benzoic acid}$$

$$B + C \xrightarrow{\text{dil. KOH}} CH_3-\underset{\displaystyle OH}{\underset{|}{C}H}-CH_2-\overset{\displaystyle O}{\overset{||}{C}}-H \xrightarrow{HCN} D \xrightarrow[\Delta]{H_3O^{\oplus}} E$$

A. Structure of A is :

(a) $H_2C=CH-CHO$
(b) $Ph-CH=CH-CH_3$
(c) $Ph-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$
(d) $Ph-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3$

B. Structure of (B) and (C) differentiated by :

(a) Tollen's reagent
(b) Fehling solution
(c) 2,4-DNP
(d) $NaHSO_3$

C. Structure of E is :

(a) HO O

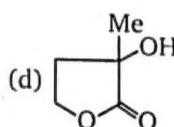
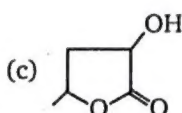
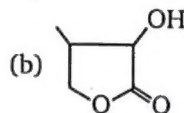
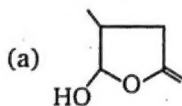
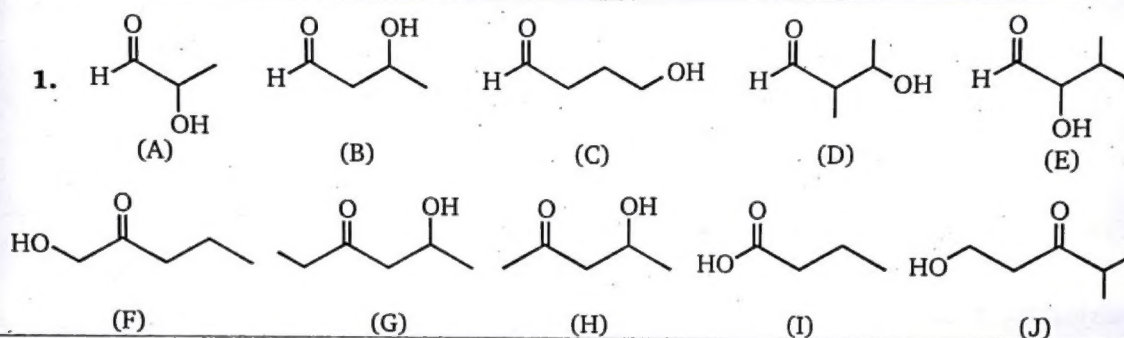
(b) OH O O

(c) OH O O

(d) Me OH O O

SUBJECTIVE PROBLEMS

1. (A) (B) (C) (D) (E)

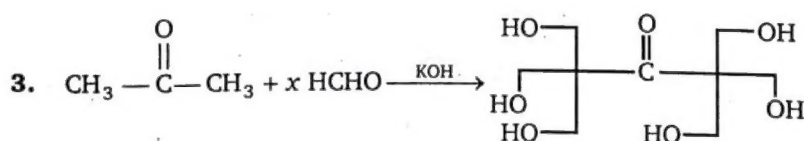
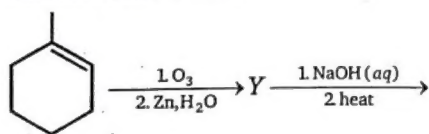
(F) (G) (H) (I) (J)

X = Number of compound obtained by aldol reaction

Y = Number of compounds react with $NaHCO_3$

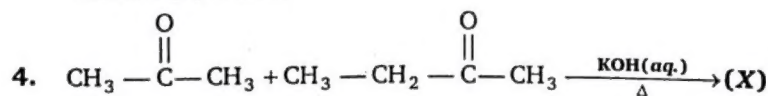
Sum of $X + Y$ is

2. In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is :

$$\xrightarrow[2.\ Zn, H_2O]{1.\ O_3} Y \xrightarrow[2\ heat]{1.\ NaOH(aq)}$$

3. $CH_3-\overset{O}{\overset{||}{C}}-CH_3 + x\ HCHO \xrightarrow{KOH}$

x = moles of HCHO consumed.

Value of (x) will be

4. $CH_3-\overset{O}{\overset{||}{C}}-CH_3 + CH_3-CH_2-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow[\Delta]{KOH(aq.)} (X)$

X = number of aldol condensation product (including stereoisomer).

Find out the value of (X).

ANSWERS — LEVEL 2

1. A – d; B – c; C – a; D – b; E – c
2. a – Donor = C, Acceptor = C; b – Donor = E, Acceptor = D;
   c – Donor = B, Acceptor = A; d – Donor = G, Acceptor = G; e – Donor = F, Acceptor = B
3. A – b; B – c; C – d; D – b; E – d
4. A – b, B – b, C – c

Subjective Problems

1. 6 **2.** 3 **3.** 6 **4.** 9